

Synthesis and properties of lead picrates

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Abstract

Picric acid is known to react with metals to form highly unstable metallic picrates, which have been implicated in a number of serious explosive accidents. In this study, lead picrates were synthesized by several methods, and the thermodynamic and explosive properties such as sensitivity were examined. Differential scanning calorimetry (DSC) results revealed that lead picrates had several heat decomposition patterns depending on the synthesis method, and they had lower temperature of start of exothermic reaction than sodium picrate had. The heat of decomposition of lead picrates was found to be lower than that of picric acid. Lead picrate from lead acetate and picric acid had lower activation energy of thermal decomposition than the other lead picrates. Thermogravimetry analysis and Karl Fischer analysis confirmed that lead picrates contained crystalline H₂O, which dehydrated at above 375 K. And, lead picrates did not have property of fusion. Drop hammer test results showed that lead picrates had high strike sensitivity, whereas the lead picrates had low friction sensitivity in friction tests, attributable to the presence of crystalline H₂O. The ignition temperatures of lead picrates were found to be in the range 543.9–600.3 K.

1. Introduction

Picric acid was used as a military explosive from World War I until the end of World War II.¹⁾ At that time, picric acid was known to react with metals to form very unstable metallic picrates, and Lea and other authors^{2,3)} attempted to synthesize these picrates. Lead picrate was said to be particularly sensitive, and was investigated by a number of groups as a primary explosive, most notably for potential use as blasting caps in Germany.²⁾ However, the interest in lead picrate was at its peak several decades ago, and only a few studies on metallic picrates (including lead picrate) employing modern analytical techniques have been conducted in recent years. Therefore, the chemical and pyrotechnic properties of these picrates were still uncertain.

In this study, lead picrate was synthesized by several methods based on the reaction as shown in Figure 1. The chemical and pyrotechnical properties of the various preparations were then examined, focusing on thermal properties. The amount of crystalline H₂O in lead picrate was also investigated as an important factor of safety,

because crystalline H₂O had been known to influence explosion sensitivity^{4,5)}. Finally, the explosion sensitivities were determined by drop hammer test, friction sensitivity test, and ignition point test.

2. Experimental

2.1 Synthesis

2.1.1 Synthesis from lead carbonate and picric acid (Pb-01)

Picric acid was obtained from Kanto Kagaku and prepared by recrystallization from a deionized H₂O solution. Lead carbonate was obtained from Kanto Kagaku and used without modification. Methanol was used as a solvent.

Lead carbonate (30 g) was added slowly to 2000 ml of picric acid solution (2.5%). Bubbles were generated in the reacting solution, attributable to by-produced carbon dioxide. The mixture was stirred for 2 h at room temperature and filtered then the unreacted lead carbonate was separated as a residue. The filtrate was then poured into a plastic vessel and concentrated under draft ventilation to approxi-

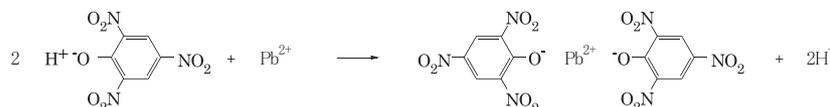


Fig. 1 Lead picrate synthesis equation.

mately 200 ml. The concentrated solution was added to dichloromethane (2000 ml) for purification to remove picric acid as a contaminant, and for recrystallization.⁶⁾ Unreacted picric acid was extracted in dichloromethane, yielding a yellow refined crystal. This synthesis procedure produced 67.2 g of final product.

2.1.2 Synthesis from lead nitrate and sodium picrate (Pb-02)

Sodium picrate was obtained from Kanto Kagaku and prepared by recrystallization from a deionized H₂O solution. Lead nitrate was obtained from Kanto Kagaku and used without modification. Deionized water was used as a solvent.

Lead nitrate (15 g) was added slowly to 500 ml of sodium picrate solution (4%), and the mixture was stirred for 2 h at room temperature. The resultant solution, which contained abundant yellow crystals, was filtered to afford crude crystals. These crude crystals were then dissolved in 300 ml of acetone, and the precipitate was filtrated. The filtrate was concentrated to approximately 100 ml and then added to dichloromethane (2000 ml) for recrystallization. The synthesis procedure produced 18.3 g of refined yellow crystals as the final product.

2.1.3 Synthesis from lead acetate and sodium picrate (Pb-03)

Sodium picrate was obtained from Kanto Kagaku and prepared by recrystallization from a deionized H₂O solution. Lead acetate trihydrate was obtained from Kanto Kagaku and used without modification. Deionized water was used as a solvent.

Lead acetate trihydrate (15 g) was added slowly to 500 ml of sodium picrate solution (4%), and the mixture was stirred for 2 h at room temperature. The resultant solution, which contained an abundant yellow precipitate, was filtered to afford crude crystals. These crude crystals were then added to 300 ml of acetone, but the crystals did not dissolve. Subsequently, the crystal was dried to give refined yellow crystals in a yield of 14.6 g of final product.

2.1.4 Synthesis from lead acetate and picric acid (Pb-04)

This synthesis method was previously attempted by Kinoshita⁷⁾ and Okumura.⁸⁾ Picric acid was obtained from Kanto Kagaku and prepared by recrystallization from a deionized H₂O solution. Lead acetate trihydrate and magnesium oxide were obtained from Kanto Kagaku and used without modification. Deionized water was used as a solvent.

Magnesium oxide (5 g) was added slowly to 1500 ml of hot picric acid solution (6.25%), followed by the addition of 180 ml of lead acetate trihydrate solution (28%). The mixture was stirred for 2 h at 333–338 K. Subsequently, the solution, which contained a precipitate, was filtered to afford crude crystals. These crude crystals were then added to 4000 ml of dichloromethane, and the mixture was stirred for purification. The resultant solution was then filtrated, and unreacted picric acid was extracted as the fil-

trate. This synthesis procedure produced 111.5 g of refined crystal as the final product.

2.1.5 Synthesis from lead oxide and picric acid (Pb-05)

Picric acid was obtained from Kanto Kagaku and prepared by recrystallization from a deionized H₂O solution. Lead oxide (PbO) was obtained from Kanto Kagaku and used without modification. Methanol was used as a solvent.

Lead oxide (15 g) was added slowly to 500 ml of picric acid solution (6%), and the mixture was stirred for 24 h at approximately 323 K. Subsequently, the solution, which contained a precipitate, was filtered to give a yellow filtrate. The filtrate was concentrated to approximately 100 ml and added to 2000 ml of dichloromethane then the mixture was stirred for recrystallization and purification. The resultant solution was then filtrated and the unreacted picric acid impurity was extracted as the filtrate. The synthesis procedure produced 34.0 g of refined yellow crystal as the final product.

2.1.6 Synthesis from lead nitrate and picric acid (Pb-06)

This synthesis method was also attempted by Urbanski.⁹⁾ Picric acid was obtained from Kanto Kagaku and prepared by recrystallization from a deionized H₂O solution. Lead nitrate was obtained from Kanto Kagaku and used without modification. Deionized water was used as a solvent.

Lead nitrate (36 g) was dissolved in 200 ml of deionized H₂O, followed by the addition of 400 ml of ice water. Picric acid (37.5 g) was dissolved in 400 ml of deionized H₂O and added to the cool lead nitrate solution. The mixture was stirred and maintained at approximately 280 K, then chilled by the addition of 200 ml of ice water to cause the product crystal to precipitate in the solution. Stirring was ceased, and the solution was allowed to precipitate for 4 h. The clear liquid above the precipitate was then decanted off, and the precipitate was filtrated out, dried and added to dichloromethane for purification to extract unreacted picric acid. The purified crystal was then dried in a vacuum at 313–333 K to ensure product stability. This synthesis procedure produced 28.0 g of final product.

2.2 Analysis

Differential scanning calorimetry (DSC) was used to characterize the thermodynamic properties of the product. DSC measurements were conducted on a TA Instruments differential scanning calorimeter, model DSC2920. Device parameters, heating and temperature properties were calibrated with respect to the fusion temperature and endothermic heat of melt of indium. The sample was sealed in an Au-evaporated aluminum crimp cell and loaded into the apparatus. The sample chamber was filled with nitrogen gas and maintained at 3 MPa. Analysis was performed on samples weighing approximately 0.5 mg at a heating rate of 10 K·min⁻¹. The measurement range was settled about 298 K to 823 K. Measurements were also conducted at heating rates of 1, 2, 5, 10, and 20 K·min⁻¹ in order to eval-

uate activation energy.

Thermal gravimetric (TG) analysis was performed in order to determine the crystalline water content of the products. Measurements were conducted using a Rigaku simultaneous thermal gravimetry and differential thermal analysis (TG-DTA) instrument, model TG8120, with infrared lamp heater. Device parameters and temperature properties were calibrated with respect to the fusion temperature of melt of indium. During measurement, the apparatus was flushed with Ar gas flowing at atmospheric pressure. The sample weight was approximately 10 mg, and the heating rate was 10 K·min⁻¹. A greater amount of sample was used for TG-DTA analysis after to ensure that the sample did not explode and damage the apparatus, and temperature of analysis was limited to 473 K. Only one analysis was performed at a higher temperature (498 K) to determine certain properties.

The crystalline H₂O content was also evaluated by the Karl Fischer method using a Metrohm 758 KFD Titrino apparatus. Riedel-deHaen Hydranal Composite 5 was used as the Karl Fischer reagent, and the machine was calibrated with approximately 30 µl of deionized water.

X-ray fluorescence spectroscopy was employed to identify the metallic elements contained in the products. Measurements were conducted using a Shimadzu wavelength-dispersive x-ray fluorescence spectrometer, model XRF 1500. Analysis of heavy elements was performed using an LiF crystal with a lattice constant (2d) of 4.0267 Å. Detection of light elemental impurities in samples (e.g., sodium) was conducted using a thallium acid phthalate (TAP) crystal.

The molecular forms of the products were analyzed by Fourier transform infrared (FT-IR) spectroscopy by the KBr method using a Shimadzu spectroscope, model FTIR-8200PC. The measurement range was 400–2000 cm⁻¹, selected so as to avoid the influence of moisture in the air.

2.3 Sensitivity tests

Strike sensitivity was evaluated by a drop hammer test, and friction sensitivity was measured by a friction sensitivity test. Both tests were performed in accordance with the Japanese standard JIS K 4810¹⁰⁾. The ignition sensitivity of ignition temperature at an ignition delay of 4 s was analyzed by an ignition point (temperature) test performed in accordance with ES-11(1)^{11,12)}.

3. Results and Discussion

3.1 Thermal analysis

Figure 2 and Table 1 show the results of DSC analysis. The exothermic decomposition curves of the lead picrates tend to be grouped in certain patterns. The thermal decomposition peaks of samples Pb-01, Pb-05 and Pb-06 were at

similar positions, the exothermic curves had similar bimodal forms. The thermal decomposition curves of other samples had different forms, and that of Pb-03 had a steep slope suggesting the occurrence of a violent reaction of exothermic decomposition. Therefore, it was estimated that the lead picrate, which was synthesized by method of Pb-03, was unstable by heating than lead picrates do from other synthesis method. Sodium picrate had steep slope of decomposition, but which was milder than result of Pb-03. This result had difference that the appearance temperature of peak of exothermic decomposition was higher than result of Pb-03, and appearance position of endothermic peak, which estimated dehydration of crystalline water, was different temperature, too. And, other lead picrates had lower temperature of start of thermal decomposition than that of sodium picrate. Consequently, it was estimated that changing of metallic element to lead, which was ionic bonded with picrate anion, was influenced to reaction temperature to be lower, and reaction was occurred more violently.

Figure 3 shows the TG-DTA analysis results. As the crystalline water properties of the as-synthesized samples changes upon exposure to air, the synthesized samples were added to deionized H₂O, and then dried in a vacuum at 298 K for 24 h. The endothermic processing of lead picrates was accompanied by a weight reduction, from which the dehydration of crystalline H₂O could be estimated. The results showed that the amount of crystalline H₂O differed depending on the synthesis method. The weight reductions began at above 375 K. As the TG-DTA analyses of other picrates (e.g., alkaline-earth metal salts and

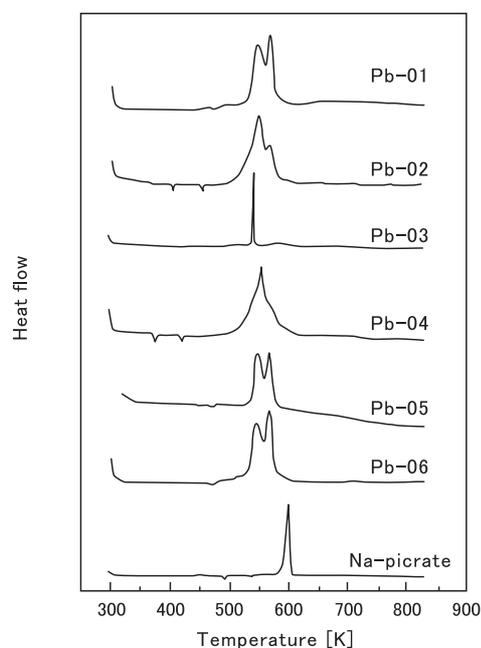


Fig. 2 DSC results for lead picrates.

Table 1 DSC results for lead picrates.

	Pb-01	Pb-02	Pb-03	Pb-04	Pb-05	Pb-06
Onset temperature [T_0]	514.1K	522.8K	536.9K	509.0K	537.3K	528.0K
Exothermic peak temperature [T_{peak}]	567.7K	549.1K	539.2K	552.6K	566.4K	565.9K
Exothermic heat	3759 J·g ⁻¹	4007 J·g ⁻¹	4818 J·g ⁻¹	3580 J·g ⁻¹	2933 J·g ⁻¹	4048 J·g ⁻¹

transition metal salts) have indicated that weight reductions start at nearly room temperature^{14,15}, it is considered that the crystalline H₂O in lead picrate is more stable than in other picrates. The analysis of Pb-03 was analyzed up to 473K, but start of endothermic phenomenon and weight reduction were confirmed nearly at the end point of analysis. Therefore, measurement was performed again, which upper temperature reset at 498K that to confirm of the reaction of nearly 473K. Consequently, it is confirmed that weight reduction and endothermic phenomenon, which estimated dehydration of crystalline water, were occurred by simultaneously at nearby 480K.

The discrepancy between the positions of endothermic peaks in DSC and TG-DTA is thought to be due to differed condition of the samples.¹⁴ In case of sample having property of fusion, the results of DSC and DTA-TG had endothermic peak at the same point, and the result of DTA-TG had endothermic peak without weight reduction. But, any sample had not such endothermic peak, therefore it was estimated that lead picrate did not have the property of fusion.

3.2 Molecular form

As shown in Fig. 4, the result of LiF x-ray fluorescence analysis revealed that the reflection patterns of all of the lead picrates were in the same positions and indicative of lead picrate. These results confirm that all of the lead picrate samples contained lead.

Figure 5 shows the results of FT-IR analysis. The results for all of the lead picrates are similar, and also similar to the results for other picrates (e.g., alkaline-earth metal salts and transition metal salts).¹³⁻¹⁸ Therefore, all of the lead picrates are considered to have almost identical molecular form.

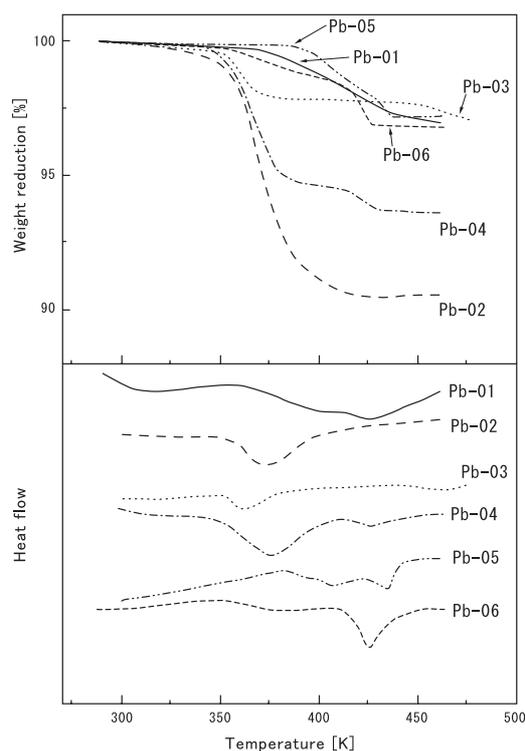


Fig. 3 TG-DTA results for lead picrates (upper column: TG, lower column: DTA).

3.3 Quantity of crystalline H₂O

Table 2 shows the results of TG analysis, and Table 3 shows the results of the Karl Fischer method. The two results do not reveal a large difference in crystalline H₂O quantity. The slight variance in the results is considered to be related to humidity in the atmosphere. It is known that the amount of crystalline H₂O in other metallic picrates changes depending on the atmospheric temperature.¹⁴ As the FT-IR results suggested that all of the lead picrates have similar molecule forms, the difference in the amount of crystalline H₂O between the present lead picrate samples appears not to be due to variations in the molecular structure.

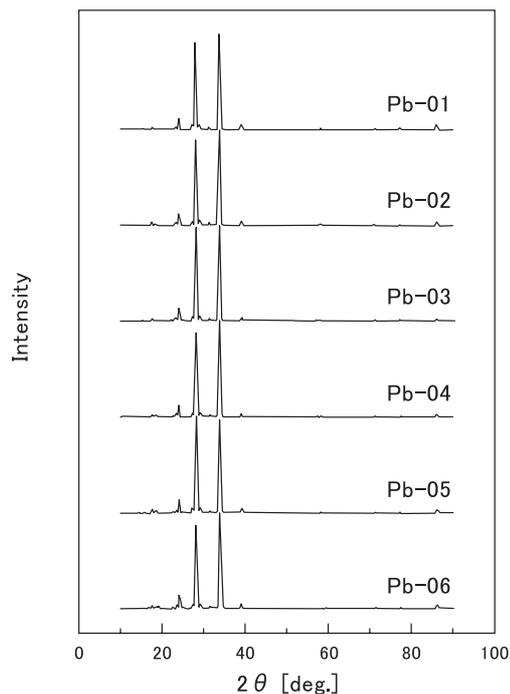


Fig. 4 X-ray fluorescence analysis results for lead picrates (spectrum crystal: LiF, wavelength range: 10–90°).

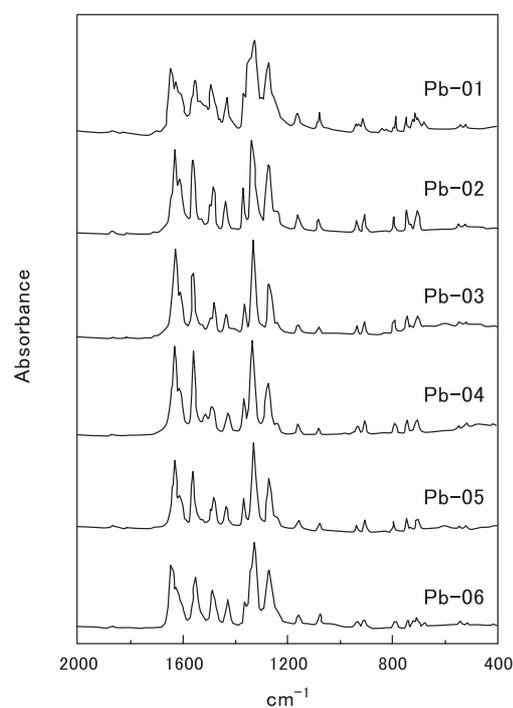


Fig. 5 FT-IR spectra of lead picrates.

Table 2 TG results for lead picrates.

	Pb-01	Pb-02	Pb-03	Pb-04	Pb-05	Pb-06
Weight reduction	3.02%	9.55%	2.89%	6.39%	2.8%	3.31%
H ₂ O molecules	1.1	3.9	1.1	2.5	1.1	1.3

Table 3 Karl Fischer analysis results for lead picrates.

	Pb-01	Pb-02	Pb-03	Pb-04	Pb-05	Pb-06	Picric Acid
H ₂ O content	2.87%	10.33%	3.16%	6.06%	2.98%	3.86%	0.22%
H ₂ O molecules	1.1	4.2	1.2	2.4	1.1	1.5	-

3.4 Yield

Table 4 shows the synthesis yields of lead picrates. The lead picrate crystals are considered to have been dried by vacuum treatment after purification. The final yield can therefore be calculated based on the crystalline H₂O content calculated using the Karl Fischer method. The molecular amount of synthesis material of sodium picrate was used as the monohydrate. The yield of Pb-06 was lower than that of the other samples at 49.8%, indicating that the reaction rate for Pb-06 was lower than for the other picrates.

3.5 Heat quantity of decomposition

The heat of decomposition of the lead picrates fell within a range of approximately 2933 - 4818 J·g⁻¹ (Table 5), lower than the heat of decomposition of picric acid, 5590 J·g⁻¹ and sodium picrate, 4834 J·g⁻¹ (13). Heat quantity of picric acid was seemed to be dropping by making of lead salt, but heat quantity per an molecule of picrate anion was more than picric acid that, except result of Pb-05. Cause of this phenomenon was estimated that reaction rate of picrate anion was improved by existent of lead element in molecule, and/or heat quantity of exothermic reaction of lead element was larger than ordinary exothermic reaction (e.g. CHNO elements).

3.6 Activation energy of thermal decomposition

The activation energies of lead picrates were obtained by the Ozawa method¹⁹⁾ (Table 6).

The DSC results were measured at 1 K·min⁻¹, 2 K·min⁻¹, 5 K·min⁻¹, 10 K·min⁻¹, and 20 K·min⁻¹, and the decomposition start temperatures (T₀) obtained from the exothermic curve of decomposition were extrapolated to determine the baseline. T₀ was plotted at each heating rate (Figure 6), and determined by Ozawa's equation.

As results of analysis, Pb-04 showed lowest result of 75.7 kJ·mol⁻¹ than other samples, therefore Pb-04 was estimated that easily to occur the thermal decomposition than other samples. But, DSC results indicated that Pb-04 had different mechanism from Pb-01, Pb-05 and Pb-06 in exothermic reaction, which was indicated in DSC result of Figure 2. The DSC analysis in Figure 2 showed that the result of Pb-01 had similar behavior of exothermic decomposition of Pb-05 and Pb-06, but experimental results clarified that Pb-01 had larger activation energy than Pb-05 and Pb-06.

3.7 Sensitivity tests

3.7.1 Strike and friction sensitivity

Table 5 lists the results of the drop hammer and friction sensitivity tests for samples pretreated in a vacuum at 298 K. The results of the drop hammer test revealed that

Table 4 Calculated yields.

	Molecular weight as anhydrate	Product amount [g]	Yield [%]
Pb-01	663.41	67.2	90.1
Pb-02		18.3	66.7
Pb-03		14.6	57.4
Pb-04		111.5	76.9
Pb-05		34.0	76.0
Pb-06		20.7	49.8

Table 5 Exothermic heat value of lead picrate (with comparison of heat as picrate anion).

	Pb-01	Pb-02	Pb-03	Pb-04	Pb-05	Pb-06
Exothermic heat	3759 J·g ⁻¹	4007 J·g ⁻¹	4818 J·g ⁻¹	3580 J·g ⁻¹	2933 J·g ⁻¹	4048 J·g ⁻¹
Exothermic heat as picrate anion molecule	5630 J·g ⁻¹	6492 J·g ⁻¹	7235 J·g ⁻¹	5560 J·g ⁻¹	4393 J·g ⁻¹	6095 J·g ⁻¹

Table 6 Results of activation energy of exothermic decomposition.

sample	Pb-01	Pb-04	Pb-05	Pb-06
Activation energy	265.0 kJ·mol ⁻¹	75.7 kJ·mol ⁻¹	195.9 kJ·mol ⁻¹	185.4 kJ·mol ⁻¹

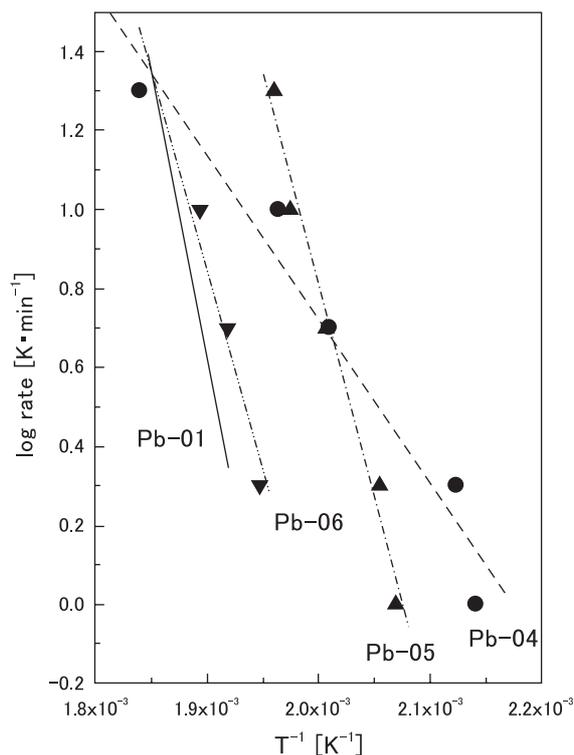


Fig.6 Ozawa's plots for decomposition start temperatures of lead picrates.

almost all samples were very sensitive to striking. The results of the friction sensitivity test revealed that the friction sensitivity of lead picrate varies depending on the synthesis method. Samples of Pb-02 and Pb-04 were less sensitive than the other samples. Pb-02 and Pb-04 had a higher crystalline H₂O content than the other samples. It is known that alkaline metal picrates with low crystalline H₂O content have high friction sensitivity,¹³⁾ whereas alkaline-earth metal picrates and transition-metal picrates are relatively insensitive to friction due to the many crystalline H₂O molecules in a picrate crystal¹⁴⁻¹⁸⁾. Therefore, the crystalline H₂O content in lead picrate is considered to influence the friction sensitivity.

3.7.2 Ignition point test

The results of the ignition point test by the Krupp method revealed that sample Pb-03 had the lowest ignition temper-

ature (543.9 K) among the lead picrates examined (Table 8). The DSC results showed that the temperature of the exothermic peak of Pb-03 was lower than that of other lead picrates, and that the exothermic curve was extremely steep. The ignition point tests appear to be directly related to T_{peak} (Table 1), except for Pb-04. Therefore, samples with low T_{peak} readily reach ignition temperature by heat conduction from the inner wall of the test rig.

Figure 7 shows the analysis results for Pb-04 which included crystalline H₂O. From observation of the reaction in the test rig for a sample containing crystalline H₂O, the solid sample first become slurry, then consolidated, and finally exploded. This behavior corresponded to dehydration to form a slurry-like mixed phase, followed by the further evaporation of moisture to form a consolidated phase, and finally explosion at a critical temperature. Due to the formation of the slurry, it was difficult to determine whether fusion was involved in the consolidation phase. The scatter in the ignition temperature results may therefore reflect of sample distribution adhered to the inner wall, resulting in differences in the effective heating and dehydration rates. Urbanski pointed that drying the samples after synthesis was important to stabilize the ignition properties of lead picrate⁹⁾. The reason of result of slightly scatters, which was Pb-04 in figure 7, was estimated that ignition point test sample of Pb-04 included full condition of crystalline H₂O.

Conclusions

A series of lead picrates synthesized by different methods was analyzed in terms of thermal properties, explosion sensitivity, and crystalline H₂O content.

- (1) All of the samples were confirmed to contain lead by x-ray fluorescence analysis, and they were identified through FT-IR analysis to have similar molecular structures.
- (2) The decomposition curves obtained by DSC analysis could be grouped into several types of patterns. The result of Pb-03 had very steep curve, it was estimated that thermal decomposition occurred violently. Picrate bonding with lead reacted more violently than that with sodium.
- (3) TG analysis revealed that crystalline H₂O dehydrates at above 375 K. The crystalline H₂O content of the samples was determined by TG analysis and the Karl Fischer method. And fusion of lead picrate was not confirmed.

Table 7 Results of drop hammer and friction tests for lead picrates.

	Pb-01	Pb-02	Pb-03	Pb-04	Pb-05	Pb-06
Drop hammer test (1/6 explosion point)	5-10 cm	<5 cm	5-10 cm	5-10 cm	<5 cm	10-15 cm
	Class 2	Class 1	Class 2	Class 2	Class 1	Class 3
Friction test (1/6 explosion point)	4.8 kgf	16-36 kgf	4-8 kgf	>36 kgf	4-8 kgf	1-2 kgf
	Class 4	Class 6	Class 4	Class 7	Class 4	Class 2

Table 8 Results of ignition temperature test for lead picrates. * t: time to ignite [s]

	Pb-01	Pb-02	Pb-03	Pb-04	Pb-05	Pb-06
Ignition temperature test (t = 4)*	563.0K	553.8K	543.9K	600.3K	569.0K	559.7K

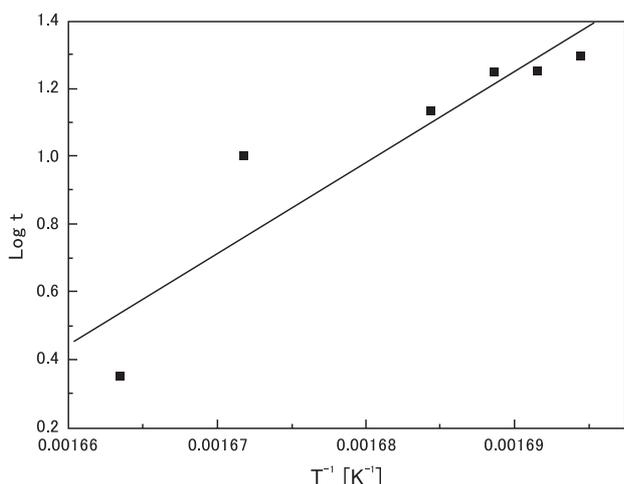


Fig. 7 Ignition temperature test results for Pb-04
(T: ignition temperature [K], t: time to ignite [s]).

(4) It was found that the heat of decomposition of the lead picrates varied widely depending on the synthesis method. Decomposition reactions of lead picrates occurred at lower temperatures than that of picric acid.

(5) Pb-04 had lower activation energy of thermal decomposition than the other samples.

(6) Drop hammer tests demonstrated that the strike sensitivity of lead picrates was quite high, and friction tests showed that lead picrates with high crystalline H₂O content had lower friction sensitivity.

(7) In ignition temperature tests, the sample synthesized from lead acetate and sodium picrate was found to be more unstable than the other samples.

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ピクリン酸鉛の合成および物性評価

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ピクリン酸は金属と反応して不安定な金属ピクリン酸塩を生成することが知られており、これまでに事故を引き起こしたことがある。本研究では、ピクリン酸鉛を数種の方法で合成し、熱的特性および爆薬としての性能(起爆感度)の試験を実施した。示差走査熱量測定の結果、ピクリン酸鉛は合成方法によって数種の分解パターンを持つことが確認され、ピクリン酸ナトリウムよりも低温で分解発熱が始まることが確認された。またピクリン酸鉛の分解発熱量は、ピクリン酸よりも低いことが分かった。酢酸鉛とピクリン酸より合成されたピクリン酸鉛は熱分解の活性化エネルギーが他のピクリン酸鉛よりも低かった。熱重量測定およびカルフイッシャー分析により、ピクリン酸鉛が結晶水を含有していることが確認され、脱水は375K以上で生起することが確認された。またピクリン酸鉛に融点は存在しなかった。落つい感度試験の結果、ピクリン酸鉛は高い打撃感度を持つことが確認されたが、摩擦感度試験の結果より、結晶水を含むピクリン酸鉛は鈍感であることが確認された。発火点試験の結果、ピクリン酸鉛の発火は543.9-600.3 Kで生起することが確認された。

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