

Synthesis and properties of alkali metal picrates

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Picric acid is known to react with metals to form highly unstable metallic picrates, which have caused serious explosive accidents. In this study, alkali metal picrates of lithium, sodium, potassium, rubidium, and cesium salts were synthesized, and the thermodynamic and initiation sensitivity were examined. Differential scanning calorimetry (DSC) results reveal that the decomposition of alkali metal picrates begins at a higher temperature than that of picric acid. The heat of decomposition of alkali metal picrates is found to be lower than that of picric acid. Thermal gravimetric analysis and Karl Fischer analysis confirm that alkali metal picrates contain crystalline H₂O. Experimental results show that the amount of crystalline H₂O in picrates is 1.0 hydrate for Li-picrate, and 1.0 hydrate for Na-picrate. However, K-picrate, Rb-picrate and Cs-picrate are anhydrate. Li-picrate mono crystal, which includes a full crystalline H₂O condition, is 3.0 hydrate in the metastable phase. The results of thermogravimetry analysis show that crystalline water dehydration occurs between 350 K and 500 K. Activation energies at start of exothermic decomposition was analyzed by different heating rates of DSC analyses. Result of analyses were; Li-picrate 127.4 kJ, Na-picrate 151.3 kJ, K-picrate 207.9 kJ, Rb-picrate 204.9 kJ, and Cs-picrate 172.8 kJ. Drop-hammer test results show that alkali metal picrates demonstrate greater impact sensitivity than picric acid. Friction test results show that anhydrate picrates show more sensitivity than hydrate picrates.

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. Metallic picrates were said to be very sensitive: examples of accidents involving metallic picrates include the detonation of metallic picrate after a metal fragment fell into burning picric acid, and the splashing of picric acid onto a metal steam pipe, which produced metallic picrate that subsequently exploded when struck.⁴⁾ In examples of industrial applications, sodium picrate was used to dye industrial materials, and potassium picrate was used as a

firework whistler and initiator.¹⁾ The risk of metallic picrate in industrial situations needs to be examined, and, hopefully, alkali picrates will be applied as a new material of pyrotechnics. In recent years, only a few studies on metallic picrates have used modern analytical techniques to examine their chemical and pyrotechnic properties.

In this study, alkali metal picrates (Li-, Na-, K-, Rb-, Cs-picrate) were synthesized from picric acid and alkali metal carbonate. Figure 1 shows the synthesis reaction, where a picrate anion bonds to an alkali metal cation. Chemical and pyrotechnical properties, but mainly thermal properties, were analyzed. Because the amount of crystalline H₂O in picrate is known to influence sensitivity^{4,5)}, this is an important safety factor. Therefore, research was conducted on the crystalline H₂O in alkali metal picrates. The results of the analyses are compared with data on picric acid properties.

2. Experimental

2. 1 Samples

Each alkali metal picrates were synthesized from a reaction of picric acid and alkali metal carbonate. Picric acid obtained from Kanto Kagaku was prepared by recrystallization from a

Received : August 11, 2003

Accepted : September 16, 2003

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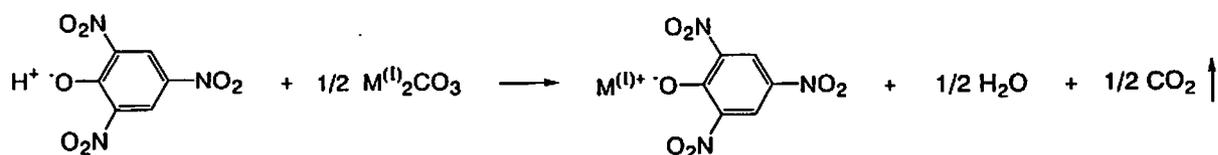


Fig.1 Alkali metal picrate synthesis equation (M means alkali metal element).

deionized H₂O solution. Metal carbonates were from Kanto Kagaku used without modification. Deionized water was used as a synthesis solvent.

2. 1. 1 Synthesis of lithium picrate (Li-picrate) from lithium carbonate hydroxide and picric acid

Lithium carbonate (7.4 g) was added slowly to 2000 ml of picric acid solution (1.15%). Bubbles were generated in the reacting solution, and these seemed to be a carbon dioxide by-product. Reaction in the solution ended quickly, and a solution became clear. The solution was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. The crude crystal was then dissolved in 100 ml of acetone, and the solution was filtrated. The filtrate was added into CH₂Cl₂ (2000 ml) for purification to remove the picric acid as a contaminant and for recrystallization. The unreacted picric acid was extracted as a filtrate.³⁾ The synthesis procedure produced 15.04 g of final product.

2. 1. 2 Synthesis of sodium picrate (Na-picrate) from sodium carbonate and picric acid

Sodium carbonate (5 g) was added slowly to 1000 ml of picric acid solution (1%). Bubbles were generated in the reacting solution, and these seemed to be a carbon dioxide by-product. Reacting solution became clear after the reaction. Solution was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. Crude crystal was then dissolved in 200 ml of acetone, and insoluble impurities were removed by filtration. Filtrate was concentrated to 100 ml, and concentrated solution was added into CH₂Cl₂ (3000 ml) for purification to remove the picric acid as a contaminant and for recrystallization. Unreacted picric acid was extracted by a method similar to that described in Section 2.1. The synthesis procedure produced 11.47 g of final product.

2. 1. 3 Synthesis of potassium picrate (K-picrate) from potassium carbonate and picric acid

Potassium carbonate (6.5 g) was added slowly to 1000

ml of picric acid solution (1%). Bubbles were generated in a reacting solution, and these seemed to be a carbon dioxide by-product. Solution became clear after the reaction. The solution was poured into a plastic vessel and condensed by draft ventilation, yielding a silky crystal in the condensed solution. Crystal was filtrated and dried. The filtrate was approximately 100 ml, and the solubility of the K-picrate in H₂O was a small amount.¹⁾ Therefore, it was estimated that a small amount of product existed in solution, and it was deposited. The crystal was then dissolved in 200 ml of acetone, and insoluble impurities were removed by filtration. Filtrate was concentrated to 100 ml and added into CH₂Cl₂ (2000 ml) for purification to remove picric acid as a contaminant and for recrystallization. Unreacted picric acid was extracted by a method similar to that described in Section 2.1, yielding a needle-like yellowish refined crystal. The synthesis procedure produced 10.6 g of final product.

2. 1. 4 Synthesis of rubidium picrate (Rb-picrate) from rubidium carbonate and picric acid

Rubidium carbonate (7.5 g) was added slowly to 1500 ml of picric acid solution (1%), and mixture was stirred for two hours. Bubbles were generated in a reacting solution, and these seemed to be a carbon dioxide product. A needle-like crystal recrystallized in the solution after a few minutes. After the reaction, the solution, which included the needle-like crystal and unreacted rubidium carbonate, was poured into a plastic vessel and dried by draft ventilation, yielding a crude crystal. Crude crystal was then dissolved in 500 ml of acetone, and insoluble impurities (e.g., unreacted rubidium carbonate) were removed by filtration. Filtrate was concentrated to 100 ml, and concentrated solution was added into CH₂Cl₂ (3000 ml) for purification to remove picric acid as a contaminant and for recrystallization. Unreacted picric acid was extracted by a method similar to that described in Section 2.1, yielding a needle-like, yellowish refined crystal. The synthesis procedure produced 19.77 g of final product.

2. 1. 5 Synthesis of cesium picrate (Cs-picrate) from cesium carbonate and picric acid

Cesium carbonate (10 g) was added slowly to a hot, 1000 ml picric acid solution (1.4%), and mixture was stirred for two hours. Bubbles were generated in a reacting solution, and these seemed to be a carbon dioxide by-product. A scaly crystal recrystallized in a large quantity. It is estimated that a solubility of the product in water was an extremely small amount. After filtration, crystal of product was dried in a vacuum chamber and dissolved in 200 ml of acetone, but precipitation was not confirmed in acetone solution. Acetone solution was concentrated to approximately 100 ml, and concentrated solution was added into CH_2Cl_2 (1500 ml) for purification to remove picric acid as a contaminant and for recrystallization. Unreacted picric acid was extracted by a method similar to that described in Section 2.1, yielding a scaly, yellowish refined crystal. The synthesis procedure produced 16.8 g of final product.

2. 2 Analysis method

Differential scanning calorimetry analysis (DSC) was used to characterize the thermodynamic properties of the product. DSC measurements were conducted on a differential scanning calorimeter, TA Instruments model DSC2920. The device parameters, i.e., the heat and temperature properties, were calibrated with respect to the fusion temperature and endothermic heat of the melting of indium. The sample was sealed in a gold-evaporated aluminum crimp cell and loaded into the apparatus, which maintains a 3-MPa nitrogen gas environment. Analysis was performed on samples weighing approximately 0.5 mg at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. The measurement range was room temperature (about 298 K) to 823 K. Measurements were also conducted at heating rates of 1, 2, 5, 10, and 20 K/min in order to evaluate the activation energy.

Thermal gravimetric (TG) analysis was performed in order to determine the crystalline water content of the products. Measurements were made with a simultaneous thermal gravimetry and differential thermal analysis (TG-DTA) instrument, TA Instruments model SDT2960. The device parameter, i.e., the temperature property, was calibrated with respect to the fusion temperature of the melting of indium. During the measurement, the apparatus was flushed with argon gas flowing at atmospheric pressure. The sample weight was approximately

10 mg, and the heating rate was $10 \text{ K}\cdot\text{min}^{-1}$. The amount of sample used for TG-DTA was more than the amount of sample for DSC. Therefore, the maximum temperature of the analysis was set at 523 K to protect the TG-DTA instrument from accidental explosion. But, in case the analysis needed a higher temperature, an end-of-analysis temperature was set at 573 K.

Crystalline water content was also investigated by the Karl Fischer method on a Metrohm 758 KFD Titrimo apparatus. Riedel-deHaen Hydranal Composite 5 was the Karl Fischer reagent, and the machine was calibrated with approximately 30 μL of deionized water.

Metallic elements contained in the products were determined by X-ray fluorescence. Measurements were made using a Shimadzu wavelength dispersive x-ray fluorescence spectrometer, model XRF 1500. Analysis of K, Rb, and Cs employed a LiF crystal having a lattice constant (2D) of 4.0267 angstroms, and analysis of Na employed a TAP (Thallium Acid Phthate) crystal.

Molecular forms of the products were analyzed by Fourier transform infrared (FT-IR) spectroscopy by potassium bromide (KBr) method, using a Shimadzu spectroscope, model FTIR-8200PC. The measurement range chosen was 400 to 2000 cm^{-1} , in order to avoid the influence of moisture in the air.

For a sensitivity test, strike sensitivity was conducted by a drop-hammer test, and friction sensitivity was conducted by a friction test. The drop-hammer and friction tests were performed in accordance with JIS K 4810.⁶⁾

3. Results and discussion

3. 1 Molecular form

As shown in Fig. 2, the result of X-ray fluorescence analysis, obtained by the TAP (Thallium Acid Phthate) spectrum crystal, reveals that Na-picrate has reflection patterns at 55.1 degrees. This pattern is characteristic of sodium X-rays. As shown in Fig. 3, the result obtained by the LiF spectrum crystal reveals that K-picrate has reflection patterns at 136.7 degrees and 118.1 degrees. These patterns are characteristic of potassium X-rays. The results shown in Fig. 4 reveal that Rb-picrate has reflection patterns at 26.6 degrees and 23.8 degrees. These patterns are characteristic of rubidium X-rays. Moreover, as shown in Fig. 5, Cs-picrate has reflection patterns at 91.8 degrees. These patterns are characteristic of cesium X-rays. The detection of the lithium element

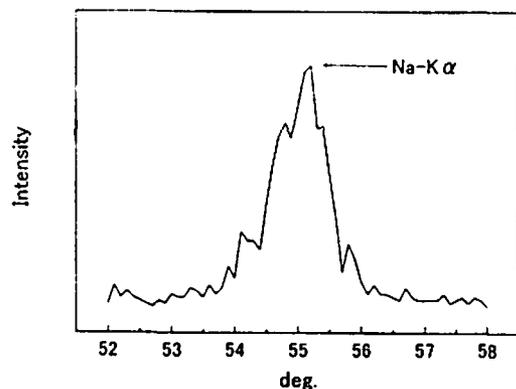


Fig.2 X-ray fluorescence analysis result for Na-picric acid (Spectrum crystal TAP, wavelength range 52-58 degrees).

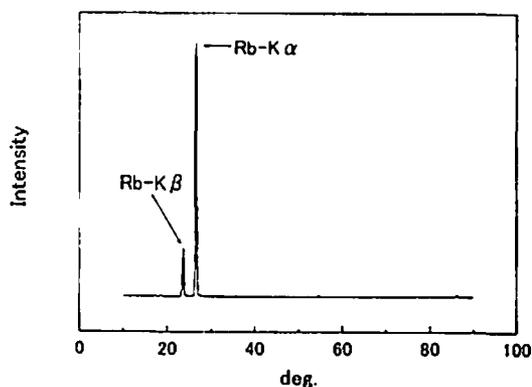


Fig.4 X-ray fluorescence analysis result for Rb-picric acid (Spectrum crystal LiF, wavelength range 10-90 degrees).

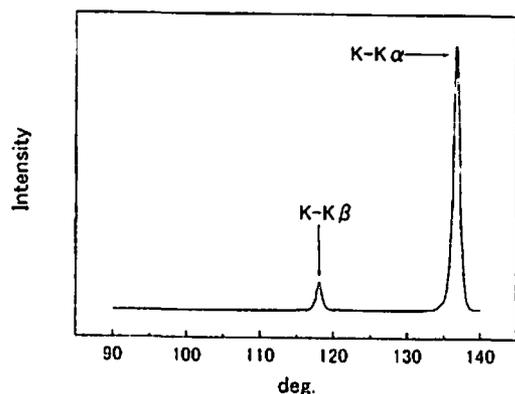


Fig.3 X-ray fluorescence analysis result for K-picric acid (Spectrum crystal LiF, wavelength range 90-140 degrees).

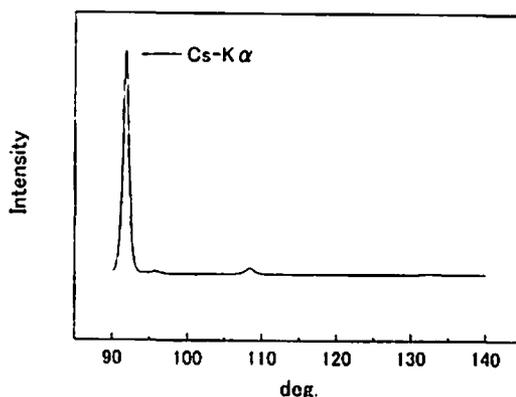


Fig.5 X-ray fluorescence analysis result for Cs-picric acid (Spectrum crystal LiF, wavelength range 90-140 degrees).

was not confirmed in the X-ray fluorescence analysis result of Li-picric acid. X-ray fluorescence analysis cannot detect the lithium element, because the wavelength of lithium is longer than the measurement limit of X-ray fluorescence analysis. But, it was confirmed that other elements besides lithium were not detected in Li-picric acid.

Figure 6 shows the results of the FT-IR analysis of all alkali metal picrates. The FT-IR results are similar for all alkali metal picrates, and also similar to the results for iron picric acid, copper picric acid, zinc picric acid and alkaline-earth metal picrates.⁷⁻¹⁰⁾ Adsorption of 1270 cm^{-1} in the FT-IR results indicates bond stretching between the phenyl group and oxygen atom. Furthermore, absorptions at approximately 1330 cm^{-1} and 1560 cm^{-1} suggest N-O bond stretching. Because the results of the FT-IR of alkali metal picrates and picric acid are very similar, alkali metal picrates are thought to have a molecular form similar to that of picric acid. Similar results have been

obtained in previous studies⁷⁻¹⁰⁾ of iron picric acid, copper picric acid, zinc picric acid and alkaline-earth metal picrates.

3. 2 Thermal analysis (DSC and TG-DTA results)

Figure 7 and Table 1 show the results of the DSC analysis. The results of the analysis show that all alkali picrates have thermal decomposition peaks that appear at higher temperatures than the decomposition peak of picric acid. For a heating rate of $10\text{ K}\cdot\text{min}^{-1}$, exothermic decomposition started at the following temperatures: Li-picric acid 582.7 K, Na-picric acid 591.2 K, K-picric acid 602.4 K, Rb-picric acid 606.6 K, and Cs-picric acid 589.4 K. These temperatures are higher than the temperature at which the exothermic decomposition of picric acid begins (542 K). Observation of the peak form reveals that the exothermic curve of the decomposition of alkali metal picrate has a steeper slope, especially for K-picric acid, Rb-picric acid and Cs-picric acid, compared to the exothermic curve of the

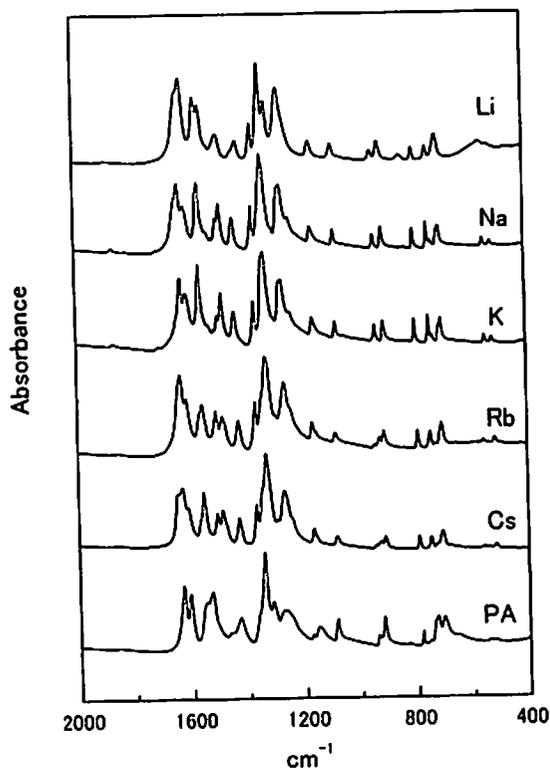


Fig.6 FT-IR spectra of alkali metal picrates and picric acid.
(Li: Li-picrate; Na: Na-picrate; K: K-picrate; Rb:Rb-picrate; Cs:Cs-picrate; PA:picric acid)

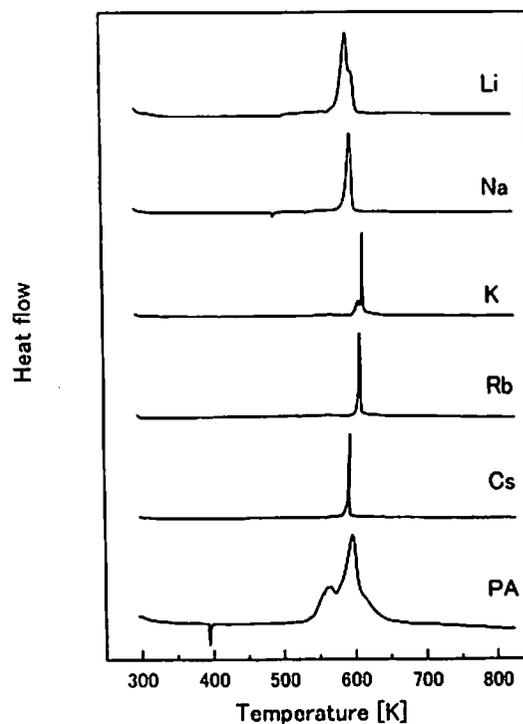


Fig.7 DSC results for alkali metal picrates and picric acid
(Li: Li-picrate; Na: Na-picrate; K: K-picrate; Rb:Rb-picrate; Cs: Cs-picrate; PA: picric acid)

decomposition of picric acid. Consequently, the production of alkali metal picrates was assumed, in which the reaction of thermal decomposition progressed rapidly. The heat of decomposition of alkali metal picrate falls within approximately $4100\text{--}5100\text{ J}\cdot\text{g}^{-1}$, which is lower than the heat of decomposition of picric acid, $5590\text{ J}\cdot\text{g}^{-1}$.

Figure 8 shows the TG-DTA analysis results. Immediately after synthesis of the crystals, the crystalline water properties are changed by refinement. Thus, the synthesized sample, which was dissolved in deionized H_2O , was recrystallized and dried in a vacuum at 298 K for 24 hours. The results of the TG-DTA of Li-picrate and Na-picrate reveal that the endothermic phenomenon

accompanied the weight reduction, and the weight reductions of Li-picrate, Na-picrate started at approximately 350 K and ended at 500 K .

Endothermic phenomenon of the DTA curve observed in Li-picrate and Na-picrate is assumed to be due to the dehydration of crystalline water at about 420 K in Li-picrate, and about 400 K in Na-picrate. These peaks indicate the dehydration of the crystalline water. The TG-DTA analysis provides the reason for this: the endothermic peak of the DTA curve corresponds with the TG curve. A weight reduction following the endothermic phenomenon was not observed for the analysis result of K-picrate, Rb-picrate and Cs-picrate. Rb-picrate had an endothermic phenomenon near the measurement-ending

Table 1 DSC results for alkali metal picrates.

	Li-picrate	Na-picrate	K-picrate	Rb-picrate	Cs-picrate	Picric acid
Start of exothermic temperature [T_0]	582.7K	591.2 K	606.6 K	589.4 K	602.4 K	522.9 K
Exothermic peak temperature [T_{peak}]	594.3 K	598.5 K	609.5 K	595.2 K	615.2 K	596.2 K
Heat of exothermic	$4369\text{ J}\cdot\text{g}^{-1}$	$4834\text{ J}\cdot\text{g}^{-1}$	$4537\text{ J}\cdot\text{g}^{-1}$	$4081\text{ J}\cdot\text{g}^{-1}$	$5073\text{ J}\cdot\text{g}^{-1}$	$5590\text{ J}\cdot\text{g}^{-1}$

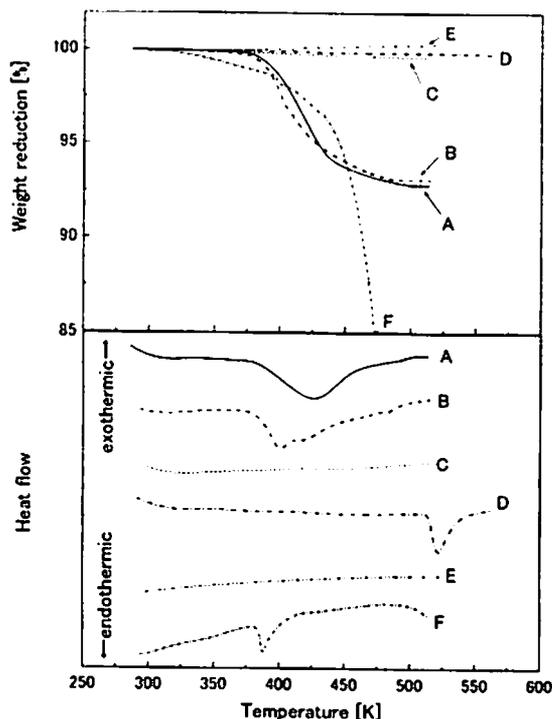


Fig8 TG-DTA results for alkali metal picrates and picric acid, (upper: TG, lower: DTA)
 A: Li-picrate; B: Na-picrate; C: K-picrate; D: Rb-picrate; E: Cs-picrate; F: Picric Acid.

temperature (523 K), but the measurement was done again after the measurement-ending temperature was reset at 573 K (Fig. 8, curve D). As a result, Rb-picrate had an endothermic peak without weight reduction at about 548 K, and the sample in the cell melted as the measurement finished. Therefore, the endothermic peak at approximately 548 K was estimated as the melting point of Rb-picrate. The endothermic phenomenon observed in the TG-DTA measurement of picric acid indicates the melting of the picric acid crystal, whereas the weight reduction beginning at approximately 430 K

indicates the decomposition or evaporation of the picric acid, or both.⁷⁾

3. 3 Quantity of crystalline water

Pretreatment of the sample crystal included pulling the sample from solution and drying it in a vacuum chamber at 298 K.

Table 2 shows the results of the TG analysis, and Table 3 shows the results of the Karl Fischer method. These results from the two different kinds of analysis method do not confirm a large difference in the quantity of crystalline H₂O.

The confirmed TG analysis results are as follows: Li-picrate with 1.0 H₂O molecules, Na-picrate with 1.0 H₂O molecules, K-picrate with 0.1 H₂O molecules, Rb-picrate with 0.0 H₂O molecules, and Cs-picrate with 0.1 H₂O molecules. Confirmed Karl Fischer method results are as follows: Li-picrate with 1.0 H₂O molecules, Na-picrate with 1.0 H₂O molecules, K-picrate with 0.0 H₂O molecules, Rb-picrate with 0.0 H₂O molecules, and Cs-picrate with 0.0 H₂O molecules. The weight reduction amount of the thermal gravimetric analysis was slightly more than the moisture amount of the Karl Fischer analysis in all samples. After the TG measurement, a yellow layer adhered to an inner wall of the sample cell and the inside of the instrument. This adhesion was thought to be due to the sublimation of heated picrate. Therefore, the reason that the amount of weight reduction in the thermal gravimetry analysis is slightly more than the moisture amount of the Karl Fischer analysis is probably because the sample weight was reduced by sublimation of the sample. The result in Table 3 shows that picric acid included a slight amount of moisture in the crystal, and it is estimated that this moisture adhered on the surface of the crystal. Karl Fischer analysis results of K-picrate, Rb-picrate and Cs-picrate are almost equal

Table 2 TG results for alkali metal picrates.

		Li-picrate	Na-picrate	K-picrate	Rb-picrate	Cs-picrate
TG	Weight reduction	7.3%	6.9%	0.39%	0.20%	0.36%
	H ₂ O molecules	1.0	1.0	0.1	0.0	0.1

Table 3 Karl Fischer method analysis results for alkali metal picrates.

		Li-picrate	Na-picrate	K-picrate	Rb-picrate	Cs-picrate	Picric acid
Karl Fischer method	H ₂ O quantity	6.9%	6.6%	0.21%	0.17%	0.22%	0.22%
	H ₂ O molecules	1.0	1.0	0.0	0.0	0.0	—

Table 4 Calculation results of yield (based on crystalline H₂O amount)

	Molecule weight as anhydrate	Crystalline waer molecules*	Product amount[g]	Yield[%]
Li-picrate	235.05	1.0	15.04	59.2
Na-picrate	251.10	1.0	11.47	97.7
K-picrate	267.20	0.0	10.60	90.9
Rb-picrate	313.58	0.0	19.8	97.2
Cs-picrate	361.01	0.0	16.8	75.8

*Crystalline H₂O value was obtained from Table 3, Karl Fischer method.

Table 5 Results of activation energy of exothermic decomposition.

	Li-picrate	Na-picrate	K-picrate	Rb-picrate	Cs-picrate	Picric acid
Activation energy	127.4K J·mol ⁻¹	151.3K J·mol ⁻¹	207.9K J·mol ⁻¹	204.9K J·mol ⁻¹	172.8K J·mol ⁻¹	144.0K J·mol ⁻¹

to the amount of moisture of picric acid, and so the moisture of K-picrate, Rb-picrate and Cs-picrate is estimated as that adhered on the surface of the crystal. Therefore, K-picrate, Rb-picrate and Cs-picrate are thought to be anhydrates.

Alkaline-earth metal picrates which include crystalline H₂O were confirmed as the devitrification of crystal from the dehydration of crystalline H₂O for a few minutes in room atmosphere.¹⁰⁾ In the case of alkali metal picrates, only Li-picrate had the property of devitrification from being placed in the room atmosphere. Li-picrate mono crystal, which had a full crystalline H₂O condition, was estimated in the metastable phase, and the amount of crystalline H₂O was measured by thermal gravimetry analysis. Li-picrate mono crystal, which was obtained in the H₂O solution, was pulled from solution and analyzed after the moisture adhering to the crystal surface was wiped off. The solution liquid, which adhered to the surface of the picrate crystal just pulled from solution, was washed by dichloromethane, and the sample was quickly placed in the analysis instrument. The result of analysis for Li-picrate, which included metastable-phase crystalline H₂O, was confirmed to have a weight reduction of 18.91%. This result shows Li-picrate includes 3.0 molecules crystalline H₂O in the Li-picrate molecule.

In the case of Na-picrate, the crystal was recrystallized to a very small silky crystal from aqueous solution; due to transparency, the crystal was not obtained.

3. 4 Yield

Table 4 shows the synthesis yields of the alkali metal

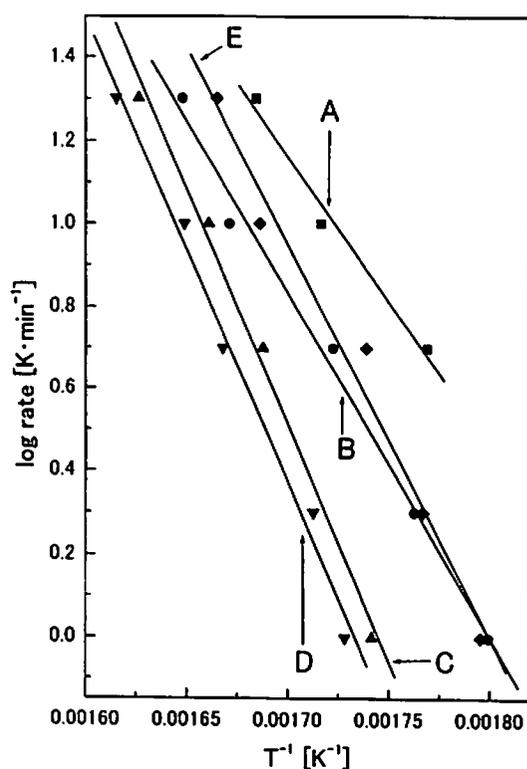


Fig.9 Ozawa's plots for decomposition start temperatures of alkali metal picrates.
A: Li-picrate; B: Na-picrate; C: K-picrate;
D: Rb-picrate; E: Cs-picrate.

picrates. Li-picrate and Na-picrate crystals were thought to have been dried by vacuum after purification, which did not include crystalline H₂O as a full condition. Therefore, crystalline H₂O was calculated by use of the Karl Fischer method in Table 3 and the picric acid amount of synthesis.

The yield of Li-picrate was 59.2%, and it was lower than that of the other picrates, but the other picrates obtained a

yield higher than 75%. Therefore, the reaction rate of Li-picrate was lower than the rate of the other picrates.

3.5 Activation energy of exothermal decomposition

The activation energies of alkali metal picrates were obtained by the Ozawa method¹¹⁾ (Table 5).

The DSC results were measured at $1\text{ K}\cdot\text{min}^{-1}$, $2\text{ K}\cdot\text{min}^{-1}$, $5\text{ K}\cdot\text{min}^{-1}$, $10\text{ K}\cdot\text{min}^{-1}$, and $20\text{ K}\cdot\text{min}^{-1}$, and the decomposition start temperatures (T_0) obtained from the exothermic curve of decomposition were extrapolated to determine the baseline. T_0 was plotted at each heating rate (Fig. 9), and determined by Ozawa's equation.

The analysis of Li-picrate, which was obtained at rates of $1\text{ K}\cdot\text{min}^{-1}$ and $2\text{ K}\cdot\text{min}^{-1}$, were performed several times, but the results were not reliable and uniform. Therefore, the analysis results of $1\text{ K}\cdot\text{min}^{-1}$ and $2\text{ K}\cdot\text{min}^{-1}$ were not used when analyzing the Li-picrate activation energy. As a result of the analysis, Li-picrate has a lower activation energy than that of other picrates and picric acid ($144\text{ kJ}\cdot\text{mol}^{-1}$), and, therefore, the thermal stability of the decomposition reaction is lower than that for the other alkali metal picrates. Meanwhile, the activation energies of K-picrate and Rb-picrate were more than $200\text{ kJ}\cdot\text{mol}^{-1}$ and higher than other picrates. Due to this fact, these picrates are estimated as having higher stability than other picrates, but the results of the differential scanning calorimetry analysis in Figure 7 show that the exothermic reaction occurred violently. Therefore, K-picrate and Rb-picrate can be estimated to be more stable when exposed high temperature than other picrates, but violently react when ignited.

As a tendency of results, the activation energy of heavy metal elements picrate is larger than light metal element picrates and picric acid. Therefore, when the picrate anion ionically bonds heavy metal of alkali element, it may cause the increase in the activation energy of decomposition.

3.6 Sensitivity test

Table 6 shows drop-hammer and friction test results for the samples that had been pretreated by vacuum drying at 298 K. The results of the drop-hammer test reveal that all alkali metal picrates are more sensitive than picric acid, or equally sensitive. Impact sensitivity was compared by species of metallic element, and the result was in order of high sensitivity; $\text{Na}>\text{Li, K, Cs}>\text{Rb}$. Factors of influence for impact sensitivity were estimated a few causes. The factor in this study may be activation energy and particle size and/or particle shape. Section 3.5 showed the activation energies of Na-picrate and Li-picrate were lower than other picrates, consequently, it can be estimated that hot spot, which occurred impact shock, was easily occurring a reaction to initiate. And, These samples had different particle size and shape. The most sensitive sample of Na-picrate was fine powder, but the most insensitive sample of Rb-picrate had large needle-like crystal shape. Consequently, it can be estimated that the impact sensitivity was influenced by size and shape of sample particle.

The results of the friction test show that K-picrate, Rb-picrate and Cs-picrate are more sensitive than Li-picrate and Na-picrate. Hopper's report⁵⁾ states that the crystalline H_2O amount in a picrate influences sensitivities. Factors of influence for impact sensitivity were estimated a few causes too. But, in this study, table 6 showing that the amounts of crystalline H_2O and friction sensitivities were had fine relation. Therefore, these anhydrous picrates (K, Rb and Cs salts) are thought to be more sensitive than hydrous picrates (Li and Na salts).

4. Conclusions

The experimental and analysis results yield the following conclusions:

- (1) X-ray fluorescence analysis results prove that the products of synthesis contain the respective elements

Table 6 Results of drop-hammer test and friction test for alkali metal picrates.

	Li-picrate	Na-picrate	K-picrate	Rb-picrate	Cs-picrate	Picric acid
Drop hammer test (1/6 Explosion point)	5-10cm	under 5 cm	5-10cm	15-20cm	5-10cm	15-20cm
	Class 2	Class 1	Class2	Class4	Class2	Class4
Friction test (1/6 Explosion point)	over 36 kgf	16-36 kgf	8-16 kgf	4-8 kgf	8-16 kgf	16-36 kgf
	Class7	Class6	Class5	Class4	Class5	Class6
Crystalline H_2O amount	1.0	1.0	0.0	0.0	0.0	-

of the synthesis subjects of alkali metal picrates. FT-IR results indicate that the products have a molecular structure similar to that of picric acid. The results show that alkali metal picrates were synthesized.

- (2) DSC analysis results of alkali metal picrates show that the decomposition reactions of alkali metal picrates occur at a higher temperature than that of picric acid decomposition, but the exothermic curves of decomposition of alkali metal picrates are steeper than that of picric acid. The heat of decomposition reactions is lower than that of picric acid.
- (3) TG analysis results of Li-picrate and Na-picrate show that crystalline H₂O is dehydrated between 350 K and 500 K. The following results of the TG analysis and the Karl Fischer method show the amounts of crystalline water in samples upon vacuum dehydration at 298 K: Li-picrate 1.0 H₂O molecules, Na-picrate 1.0 H₂O molecules. K-picrate, Rb-picrate and Cs-picrate are anhydrate. Crystalline H₂O in the full-included condition of Li-picrate is 3.0 H₂O molecules.
- (4) Thermal analysis shows the melting point of Rb-picrate is approximately 548 K.
- (5) Activation energies at start of exothermic decomposition of alkali metal picrates were analyzed by different heating rates of DSC analyses. Result of analyses were; Li-picrate 127.4 kJ, Na-picrate 151.3 kJ, K-picrate 207.9 kJ, Rb-picrate 204.9 kJ, and Cs-picrate 172.8 kJ.
- (6) Drop-hammer test results show that the strike sensitivities of alkali metal picrates are more sensitive than those for picric acid, or equally sensitive. Friction test results show that anhydrous picrates are more sensitive than hydrate picrates.

Acknowledgements

This study was conducted under the auspices of the ACW office of the Cabinet Office and the Japan Institute of International affairs.

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