

The synthesis of iron picrates

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This paper reports the chemical properties of iron picrate synthesized by two different methods. Differential scanning calorimetry analysis shows the decomposition of iron picrate starts at a lower temperature than that of picric acid, and the heat of exothermic reaction for iron picrate was less than that of picric acid. The iron ion valence in iron picrate that is synthesized by the method of this study is Fe^{2+} . The results of elemental analysis and thermogravimetry show that the hydrate of iron picrate is hexahydrate to octahydrate. Dehydration of combined H_2O occurs between 300-400K. Iron picrate is synthesized not only by the reaction of other picrate with iron salt, but also by the reaction of picric acid solution with iron powder.

1. Introduction

Picric acid was used as a military explosive from World War I till the end of World War II¹⁾. At that time, it was known that picric acid reacts with metals to form very unstable metallic picrates. Indeed, lead picrate had been studied for use as a primary explosive of detonators in Germany²⁾.

Due to an assumption of accidental outflow of the picric acid in environmental, it forms the iron picrate when it contacts with iron. While iron picrate has been used as a fuel additive³⁾⁴⁾, few studies have so far been carried out on the mechanism of synthesis and the chemical and pyrotechnics properties. In this study, iron picrates were synthesized using two methods: the reaction of iron powder with picric acid solution, and the reaction of iron sulfate ($FeSO_4$) with barium picrate solution⁵⁾. The products were then investigated to

find whether they have similar properties.

2. Experimental

2.1 Synthesis of iron picrate from iron powder and picric acid (Iron picrate A)

Picric acid was obtained from Kanto Kagaku. It was prepared by recrystallization from deionized H_2O solution. Iron powder was obtained from Wako Pure Chemical Industries, Ltd. It was used as received. Deionized water was used for the synthesis solvent.

Picric acid was dissolved into H_2O (500ml), and the quantity of picric acid was enough to make a saturated picric acid solution. Iron powder (200mesh:20g) was added slowly to the saturated picric acid solution and the mixture was stirred for 2 spare hours at room temperature. pH variation of the solution was measured for confirmation of the end of reaction. The pH of solution turned to pH 6 at the end of reaction. The reacted solution was filtered and precipitation of unreacted iron powder was separated. The filtrate was heated and condensed until the quantity of the solution reached approximately 200ml and was poured into a plastic vat. The solution was dried with ventilation in a draft and the black crystal was obtained as product. Synthesized iron picrate was purified with dichloromethane in order to

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extract the contamination of unreacted picric acid in the filtrate⁶⁾.

2.2 Synthesis of iron picrate from iron sulfate (II) and picric acid solution (Iron picrate B)

In this method, iron picrate was synthesized by way of barium picrate as intermediate. Barium picrate was prepared from picric acid and barium carbonate in deionized H₂O⁷⁾. The quantity of barium carbonate was used for equivalent to react with the saturated solution of picric acid 500ml. Ferrous sulfate (FeSO₄) was added into the barium picrate solution and stirred for 2 hours⁵⁾. Barium sulfate as precipitation of by-product was filtered and separated. The filtrate was heated and condensed until the quantity of the solution reached approximately to 200ml and poured into a plastic vat. The solution was dried with ventilation in a draft and a yellow crystal was obtained as product. The contamination of unreacted picric acid was extracted by a similar method to the above.

2.3 Analysis method

Differential scanning calorimetry analysis (DSC): DSC measurements were performed using a TA INSTRUMENTS DSC2920 differential scanning calorimetry apparatus. The apparatus was calibrated based on melting point and heat of fusion of indium. The sample was sealed into an aluminum crimp cell and an atmospheric condition in the apparatus was kept with 3 MPa pressurized by nitrogen gas. The sample weight was about 1mg and heating rate was 10 K·min⁻¹.

Thermogravimetry (TG): The TA Instruments SDT2960 Simultaneous TGA-DTA apparatus was used to determine the quantity of combined H₂O in the products. Experiment was carried out under Ar gas stream. Sample weight was about 1mg and the heating rate was 20 K·min⁻¹.

Elemental analysis: Elemental analyses were carried by a Perkin Elmer 2400 Series II CHNS/O Analyzer.

X-ray fluorescence analysis: The existence of iron was determined by a Shimadzu XRF-1500 wavelength dispersive x-ray fluorescence spectrometer.

Fourier transform infrared spectroscopy analysis

(FT-IR): IR spectra were obtained by a Shimadzu FTIR-8000PC Fourier transform infrared spectroscopy apparatus. The sample was prepared by the KBr method.

Detection of iron ion valence: Iron ion valence was conveniently identified by reagent color reaction, in which potassium hexacyanoferrate (III) turns to blue in existence of Fe²⁺ ion and ammonium thiocyanate turns to red in existence of Fe³⁺ ion.

3. Results and discussion

3.1 Thermal analysis

The samples that were synthesized by both methods were analyzed by DSC. The exothermic decomposition of samples iron picrate was started at approximately 473K (Fig.1). Both decomposition temperatures were lower than that of picric acid which was approximately 540K. The exothermic heat of iron picrate was 4000 to 4100 J·g⁻¹, which is less than the approximate value of 5400 J·g⁻¹ of picric acid. The exothermic decomposition behaviors of both samples above exothermic reaction were very similar to each other, which

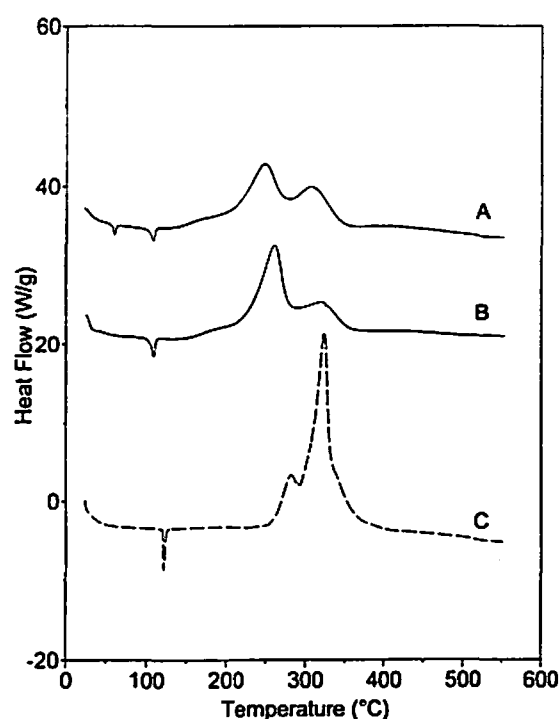


Fig. 1 DSC results for iron picrate and picric acid
A; synthesized from picric acid and iron powder,
B; synthesized from barium picrate and ferrous sulfate,
C; picric acid (KANTO Kagaku)

was suggested that similar reactions occurred in both decomposition process. But, whether the endothermic peak around 330K appears or not depended on synthesis method. The reason of this difference was speculated as to ascribe additional state of combined H₂O.

3.2 Molecules form of iron picrate

The result of X-ray fluorescence analysis shows the products from each synthesis method had characteristic K α peaks of iron, which indicates the existence of iron element.

Adsorption of 3100cm⁻¹ of FT-IR exhibits C-H stretch bonding, and 1330~1340cm⁻¹ and 1530~1560cm⁻¹ absorption exhibit N-O stretch bonding (Fig.2). The results of FT-IR by iron picrate and picric acid were very similar to each other, except that iron picrate had a absorption around 1480cm⁻¹. Therefore, iron picrate molecule form was estimated to have a similar molecule form to picric acid. 3000-3600cm⁻¹ broad peak indicates O-H stretch bonding. This peak of iron picrate was larger than the peak of picric acid because iron picrate had 6-7 molecules of H₂O as hydrate (see below for further details) and picric acid had only single O-H bonding.

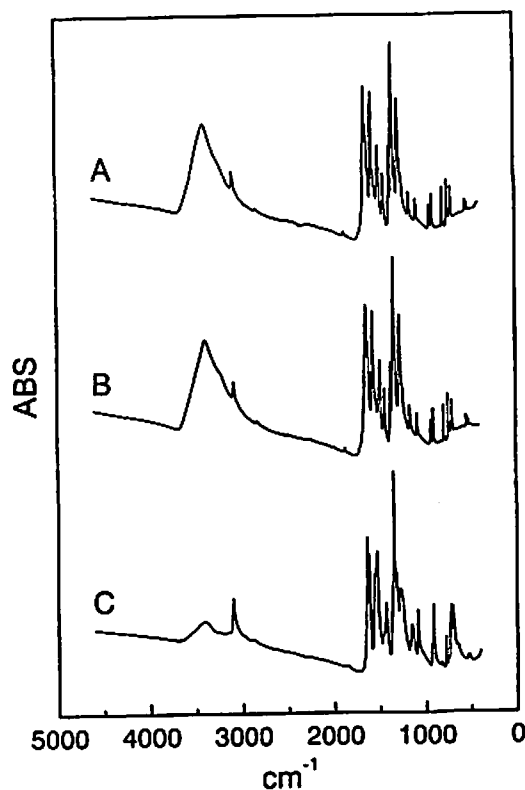


Fig. 2 FT-IR spectra of iron picrates (A, B) and picric acid

- A; synthesized from picric acid and iron powder,
- B; synthesized from barium picrate and ferrous sulfate,
- C; picric acid

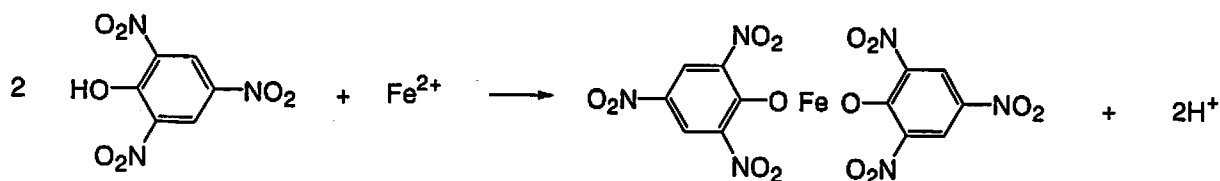


Fig. 3 Chemical reaction and form of iron picrate molecule

Table 1 shows the results of elemental analysis, however results of elemental ratio of oxygen and iron were calculated based on result of carbon quantity, and the quantity of combined H₂O was calculated based on result of hydrogen quantity. The results of species and numbers of element were estimated for molecules of two piece picrate anion. Therefore, it was confirmed that iron picrate had the form of an iron cation with two molecules of picrate anion (Fig. 3), which were the same results for the samples obtained by both synthesis methods. Table 2 shows the results of coloring test for detection of iron ion valence, which indicate

the existence of Fe²⁺ ion in the sample and the absence of Fe³⁺ ion.

3.3 Water of crystallization in iron picrate

TG analysis results are shown in Fig.4. Weight reduction occurred gradually from about at 300K, and ended about at 400K. The result of trace A in Fig. 4 shows that sample from picric acid and iron powder reduced weight by 18.45%, which was equal to 6 molecules of H₂O. Consequently, the sample was estimated to be hexahydrate. The result of trace B in Fig. 4 shows that sample from barium picrate and ferrous sulfate reduced weight by

Table 1 Elemental analysis result of iron picrate

Element	Atomic Weight*	Iron picrate A Picric Acid + Iron powder		Iron picrate B Barium picrate + FeSO ₄	
		results** (wt.%)	element ratio***	results** (wt.%)	element ratio***
C	12.01	22.59	12	22.08	12
H	1.01	2.55	16	2.57	16
N	14.01	12.59	6	12.70	6
O****	16.00	50.29	20	49.84	20
Fe****	55.85	8.75	1	8.56	1
Combined H ₂ O*****		6.05		6.06	

*Quotation from NIST Standard Reference Database 69 (2001)

**Results included the quantity of combined H₂O molecules

***Calculate base: C=12

****Oxygen and iron element ratio were calculated by based on result of carbon quantity

*****The quantity of combined H₂O was calculated by based on result of hydrogen quantity

21.02%, which was equal to 8 molecules of H₂O. Consequently, the sample was estimated to be octahydrate. This result was different from result of elemental analysis (Table 1). This reason was estimated that the sample for TG analysis was just after synthesis. Iron picrate was liberated 2 H₂O molecules within several days after the synthesis, which was stable phase of hexahydrate in room

Table 2 Result of reagent color reaction

	coloration		result
	Potassium hexacyanoferrate (III)	Ammonium thiocyanate	
Picric Acid + Iron powder	Blue	colorless	Fe ²⁺ exist
Barium picrate + FeSO ₄	Blue	colorless	Fe ²⁺ exist

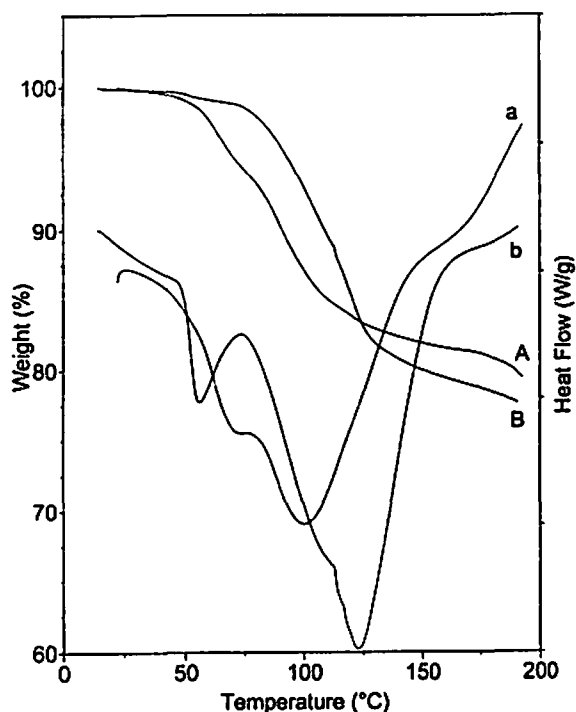


Fig. 4 DTA and TG curves of iron picrate
A(TG) and a(DTA); iron picrate synthesized
from picric acid and iron powder.
B(TG) and b(DTA); iron picrate synthesized
from barium picrate and ferrous sulfate.

temperature. Consequently, the water of crystallization in iron picrate was metastable phase at just after synthesis. The difference in TG traces of each sample at approximately 330K was ascribed to the similar reason of difference in DSC traces.

The results from elemental analysis are similar to that of TG. Each iron picrate had 6 molecules of combined H₂O (Table 1).

Conclusions

From the experimental and analysis results, the following conclusions can be obtained:

- (1) The result of X-ray fluorescence proved iron element existence in synthesized products, and FT-IR results indicated that the products had similar molecule form of picric acid. Regardless of difference in synthesis method, it is shown that iron picrate was synthesized.
- (2) Based on coloring test, Fe²⁺ ion was detected in both iron picrates.
- (3) The results of TG analysis and elemental

analysis showed the products were hexahydrate at stable phase in room temperature.

- (4) Iron picrate was synthesized from picric acid solution and iron powder. The appearance of products was different from each other, but their chemical properties were resembled. Consequently, it was proved that iron picrate was synthesized not only by the reaction of other picrate (ex. barium picrate) with iron salt, but also by the reaction of picric acid solution with iron powder.

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