

Thermal hazard of iron picrate

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Abstract

Iron picrate (FePic) was synthesized under conditions similar to those that result in the natural deterioration of chemical weapons. Its thermal hazard was investigated by comparing it with iron picrate obtained by the chemical synthesis method (FePic(Ba)).

FePic has eight or more water molecules of crystallization and consists of a mixture of various hydrates. It shows low sensitivity to friction and drop hammer tests due to the large number of water molecules of crystallization. Under the experimental conditions of the thermal analysis, the hydrated iron picrates began to decompose before being dehydrated to form the anhydrous salt. Prolonged holding under natural environmental conditions does not appear to result in formation of the dangerous anhydrous salt.

Based on the observed heating rate dependence, it is thought that the hydrated iron picrate should start to decompose before dehydration to the anhydrous salt occurs when subjected to a large heating rate.

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1. Introduction

Picric acid is an explosive substance used in military applications such as bursting explosives and boosters. Some of the chemical weapons abandoned by the Japanese army in China during World War II were of this type. The shells of these chemical weapons may have undergone corrosion due to the length of time they have been buried underground. It is suspected that the corroded iron has reacted with the picric acid contained in the weapons, resulting in the formation of iron picrate, which is likely to be more hazardous than free picric acid.

The properties of metal picrates were investigated during the latter part of the nineteenth century and the early part of the twentieth century [1–3]. Silberrad and Phillips reported the explosion temperatures of a large number of anhydrous metal picrates [1]. Kast studied the sensitivity to impact of picrates with varying water-of-crystallization ratios [3]. Tucholski performed thermal analysis of various metal picrate hydrates [2]. The metal picrates used in these investigations were generally prepared as metal picrate hydrates from aqueous solution and were dehydrated by

heating at temperatures of 80–150 °C. A small number of iron picrate hydrates were included in these reports. The main conclusion of these studies was that anhydrous metal picrates are capable of vigorous detonation when subjected to heat or shock. Recently, the gaseous products resulting from flash pyrolysis of metal picrate salts were investigated as an energetic material; the metals studied were Li, Na, K, Rb, Cs, Co and Ni [4,5]. When disposing of a chemical weapon, knowledge of the type of metal picrate hydrate generated after deterioration, its thermal character and its explosion characteristic may reduce the risk of explosion during treatment.

In this study, iron picrate was synthesized under conditions close to those under which a chemical weapon may deteriorate naturally. The atmospheric conditions were decided by reference to annual climate records in China. The thermal behavior of the picrate was investigated by comparing it with the salt obtained by chemical synthesis.

2. Experimental

2.1. Synthesis of iron picrate

The iron picrate used in these experiments was synthesized by two methods. In the first, 20 g of iron powder was added to

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500 ml of saturated picric acid solution with stirring ($C=0.01$ g (picric acid) ml^{-1}). After adjustment of the pH from 1 to 6, the solution was filtered to remove the unreacted iron powder. The solution was condensed under vacuum and then poured into a plastic vessel. The iron picrate thus precipitated was washed with dichloromethane and dried in air. The conditions under which the synthesis took place were similar to those resulting in the natural deterioration of a chemical weapon. The average temperature was kept above 28°C and the humidity was adjusted to a level between 43 and 90%. These conditions were decided by reference to annual climate records in china. The salt obtained by this method is referred to as FePic.

Iron picrate was also synthesized from barium picrate based on the method proposed by Silberrad and Phillips [1]. Barium carbonate (3 g, 0.011 mol) was added to 400 ml of picric acid solution ($C=0.0625$ g (picric acid) ml^{-1}) with stirring. After filtration of the solution to separate the unreacted barium carbonate, 1.52 g of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.055 mol) was added to the filtrate. The resulting solution was again filtered to separate barium sulfate. The solution was then condensed under vacuum and poured into a plastic vessel. The iron picrate thus precipitated was washed with dichloromethane and dried under controlled conditions; atmospheric temperature was around 28°C and humidity was adjusted to 60%. The salt obtained by this chemical method is referred to as FePic(Ba).

2.2. Thermal analysis

Differential thermal analysis and thermogravimetric analysis (DTA–TG) were carried out using a TA instrument, the DSC 2920 Thermal Analyzer. The sample container was an aluminum cell; it was confirmed that aluminum did not affect the reaction by the preliminary experiment. The sample (1 mg) was heated to 500°C at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 . In order to derive kinetic information, samples were heated from room temperature to 500°C using heating rates ranging from 2 to $20^\circ\text{C min}^{-1}$, according to the ASTM E698 method [7].

Differential scanning calorimetric measurements were performed using a TA instrument, the DSC 2960 Thermal Analyzer. Measurements were carried out under various pressures in the range 0.1–3 MPa.

2.3. Atmospheric control

The sample was held in a vacuum chamber in which controlled heating was possible. The humidity was adjusted using saturated solutions of various salts such as ammonium chloride. In order to investigate the influence of humidity, samples were held under high humidity after dehydration at 55°C ; the temperature was held at 28°C and the humidity was adjusted to 70%. Samples were also kept under a comparatively dry atmosphere to investigate the likelihood of dehydration to the anhydrous salt in the natural environment. For this, the temperature was held at 30°C and the humidity adjusted to 33%. After the stipulated period, which ranged from several hours to 2 months, thermal analysis was carried out under the measurement conditions described in Section 2.2.

2.4. Sensitivity control

Both salts were subjected to the BAM friction test and the drop hammer test, which were conducted according to the JIS K4810 method [6].

In the friction test, the sample capacity was about 0.01 ml and friction force was applied using various loads. In the drop hammer test, sample capacity was about 0.01 ml. A 5-kg ball was dropped from various heights: 5, 10, 15, 20, 30, 40 and 50 cm.

Both tests were performed six times on each salt and after each test the sample was checked for ignition.

3. Results and discussion

3.1. Iron picrates

The iron picrates obtained from the two synthesis methods appeared to be different, as shown in Photo 1. FePic(Ba) was obtained in the form of transparent yellow crystals, while FePic was mainly brown and non-uniform. The FePic(Ba) crystals grew in the form of very fine needles, similar to those of coniferous trees. On the basis of single crystal X-ray diffraction, Honda et al. reported that the iron picrate salt synthesized from barium picrate was a six-coordinated octahedron [6] with six water molecules coordinated to iron. Rather than being attached to the iron, the picric anion participates in charge neutralization. In this study, the same results were obtained for FePic(Ba) using single crystal X-ray diffraction. FePic(Ba) was shown to be an iron picrate with eight hydrates. However, single crystal X-ray analysis was not performed for FePic due to the difficulty of obtaining a single brown crystal of this salt.

Fig. 1 shows the Raman spectra of both salts, with that of picric acid also shown for reference. Nitro-group symmetric and antisymmetric stretching vibrations were confirmed at 1350 and at 1500 – 1530 cm^{-1} , respectively. There are few differences between the FePic and the FePic(Ba) spectra, but they are both different from that of picric acid.

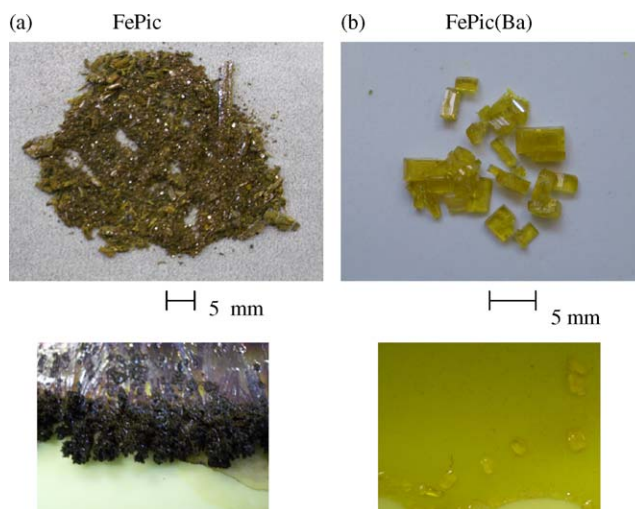


Photo 1. Photograph of iron picrate.

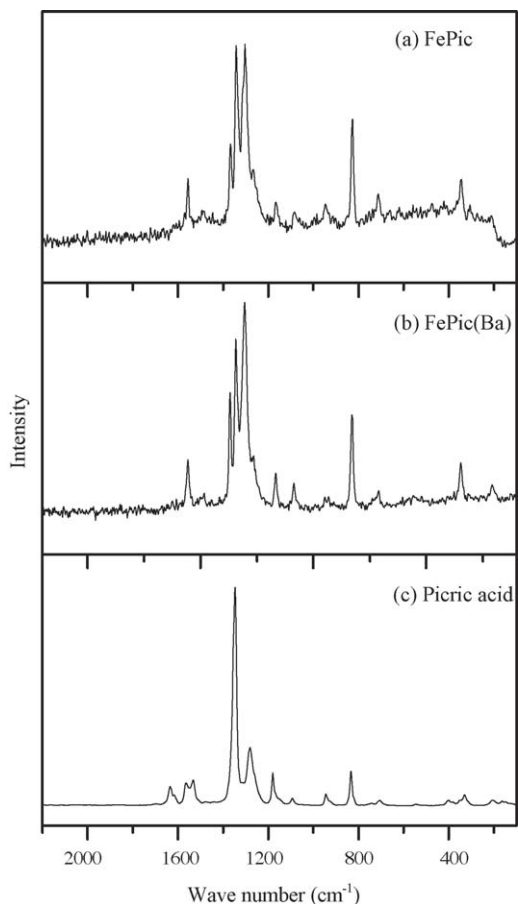


Fig. 1. Raman spectra of iron picrate salts.

In the friction test, both salts failed to ignite on six or more occasions using a load of 36 kgf. In the drop hammer test, both salts failed to ignite on six or more occasions when a 5-kg ball was dropped from a height of 50 cm. The low sensitivity of both salts in the friction and drop hammer tests may be due to the presence of a large number of water molecules of crystallization. Kast reported that ferrous picrate kept at 100 °C detonated every time when a 2-kg ball was dropped from a height of 25 cm six times [2]. The iron picrate kept under vacuum (dihydrate) seemed to emit smoke and did not detonate when a 2-kg ball was dropped from a height of 30 cm.

3.2. Thermal analysis

Fig. 2 shows the results of thermal analysis of the two iron picrates. Both began to decompose exothermally at 171 °C after exhibiting endothermic peaks up to 150 °C due to dehydration. The presence of these endothermic peaks confirmed that both salts contain a large number of water molecules of crystallization.

The gravimetric change at 287 °C was very vigorous and resulted in the sample being scattered. Tucholski reported that the octahydrate iron picrate gradually released water molecules to form an anhydrous salt that decomposed at 296.5 °C [2]. In our experiment, the anhydrous salt may have been partially formed

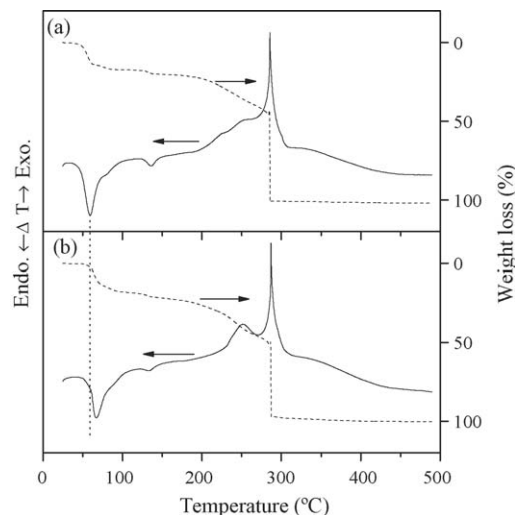


Fig. 2. DTA–TG curves of iron picrate: (a) FePic and (b) FePic(Ba).

during the decomposition process, based on the vigorous reaction at 296.5 °C under the experimental conditions of the thermal analysis.

The dehydration mechanism was predicted on the basis of weight loss in FePic(Ba), which consisted of uniform crystals. The weight loss ratios were 6 and 1 for endothermic peaks at or below 100 °C and at approximately 130 °C, respectively. The number of water molecules of crystallization changed from eight to two, and then from two to one. This result is different from that obtained by Tucholski, who reported that the number of water molecules of crystallization changed from eight to four, and then from four to zero [2]. According to the results of X-ray single crystal analysis [7], the six water molecules that disappeared first were those coordinated to iron. In the case of FePic(Ba), the monohydrate appeared to decompose at 170 °C before dehydrating into an anhydrous salt during the decomposition at a heating rate of 10 K/min.

It can be seen that FePic has a greater number of water molecules of crystallization than FePic(Ba), because the first endothermic peak was observed at a lower temperature. Changes in endothermic peak behavior depending on the portion of the sample used showed that FePic was actually a mixture of various hydrates. Changes in synthesis conditions, including variations in the amount of water used and the degree of condensation, did not affect salt formation: brown, not yellow, crystals were formed. Conditions similar to those under which the natural deterioration of chemical weapons takes place appeared to encourage the formation of a salt containing eight or more water molecules of crystallization. However, no detailed investigation has been carried out in this regard.

The DTA curve showed that FePic also seemed to decompose before dehydrating into an anhydrous salt during decomposition at a heating rate of 10 K/min.

Fig. 3 shows the pressure dependence of the decomposition of the two iron picrates. This pressure dependence was confirmed in the case of FePic. The dehydration mechanism was also thought to be different for each salt, although the endothermic peak

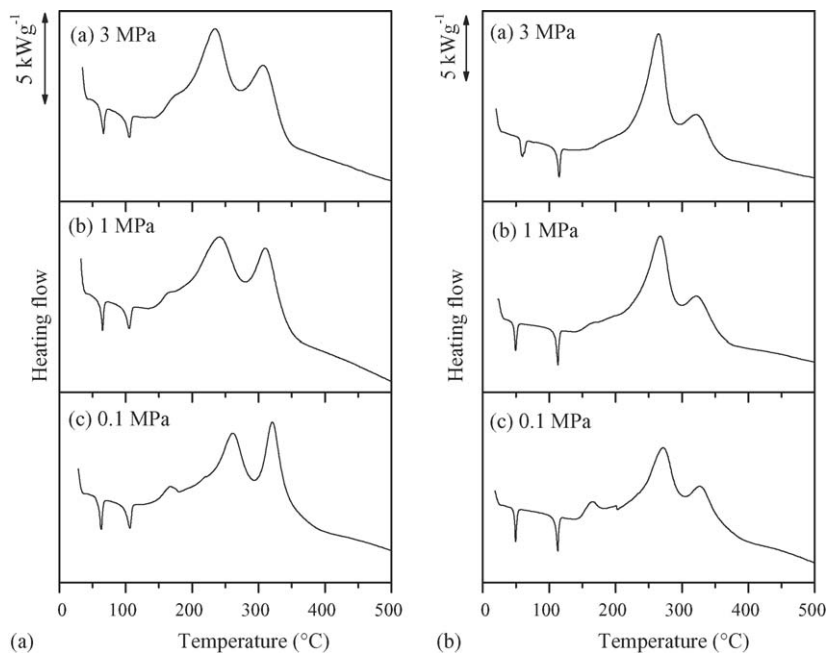


Fig. 3. DSC curves of iron picrate at various pressures. (a) FePic and (b) FePic(Ba).

temperatures were clearly different. The heat of decomposition, which was above 3400 J g⁻¹, was the same for both salts.

3.3. The effect of atmospheric control on FePic

We attempted to investigate the influence of atmospheric conditions on the reactions of the FePic salt. Initially, the sample was kept under 70% humidity after being held at 55 °C under vacuum for several hours. Fig. 4 shows the thermal analysis results of this experiment. The endothermic peak obtained at approximately 55 °C disappeared after the salt was held at 55 °C under vacuum for 15 h. After holding the salt under 70% humidity, as shown in Fig. 4(d), this peak reappeared. Fig. 5 shows DTA curves and weight loss curves obtained while the salt was held under 70% humidity. Fig. 6 shows the change in weight loss

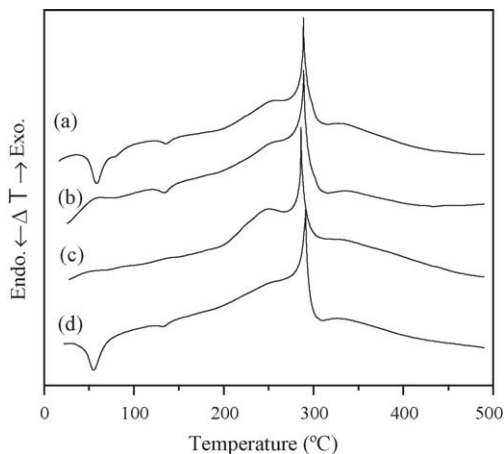


Fig. 4. DTA curves of iron picrate after holding under various conditions. (a) FePic, (b) at 55 °C, under vacuum for 15 h, (c) at 100 °C for 5 days and (d) in 70% humidity after (b).

value of the peak at 55 °C. The weight loss converged to 15% and was maintained at a fixed value, which was the same as the original value, after approximately 220 h. The same result was obtained by holding the salt under 85% humidity. Equilibrium was established under these conditions of high humidity and stable hydrates were formed. Salts do not necessarily absorb an infinite amount of moisture.

Next, the sample of FePic was held in a comparatively dry atmosphere, at 30 °C and 33% humidity. As shown in Fig. 7, the endothermic peaks at or below 80 °C were observed even after the sample had been held under these conditions for 35 days. The

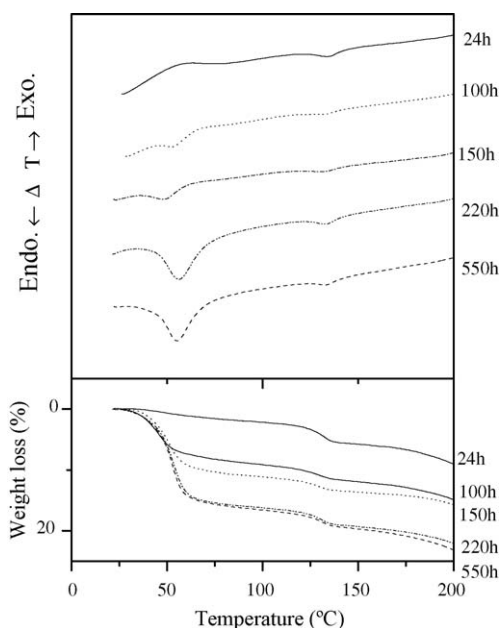


Fig. 5. DTA and weight loss curves obtained while the salt was held under 70% humidity after the dehydration.

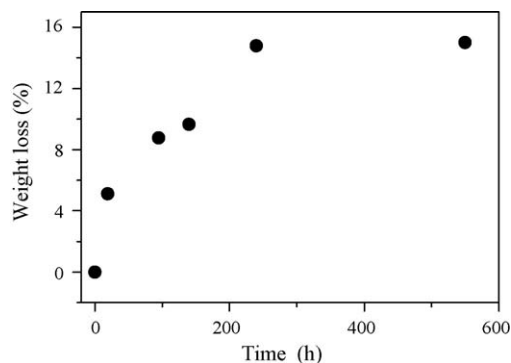


Fig. 6. Weight loss change in the endothermic peak at 55 °C.

shoulder peak at 55 °C increased gradually. This implies that iron picrate that has undergone corrosion is not easily dehydrated in the natural environment to yield the dangerous anhydrous salt. In FePic, the water molecules were not released to form the anhydrous salt even when the sample was maintained at 100 °C for 5 days (Fig. 4c). Kast reported that after several hours at 100 °C, the eight water molecules of iron picrate were released to form the anhydrous salt [3].

The formation of the anhydrous salt of iron picrate via dehydration was not confirmed in this experiment. It is thought that the anhydrous salt may be formed only under strict conditions in the laboratory.

3.4. Dependence on heating rate of thermal behavior

Figs. 8 and 9 show the dependence of thermal behavior on heating rate for both iron picrates. As the heating rate decreases, all the peaks shift toward lower temperatures. Each picrate displays different thermal behavior. In the case of the FePic(Ba) salt, an increase in the heating rate results in the clear separation

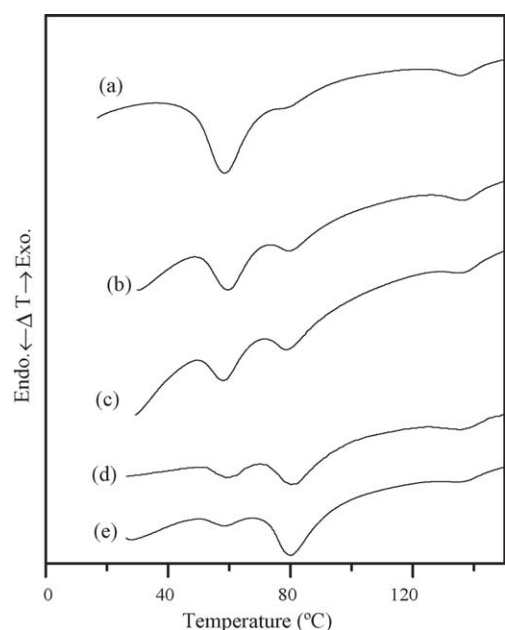


Fig. 7. DTA curves of FePic after holding at 33 °C in 30% humidity. (a) 0 days, (b) 15 days, (c) 29 days and (d) 35 days.

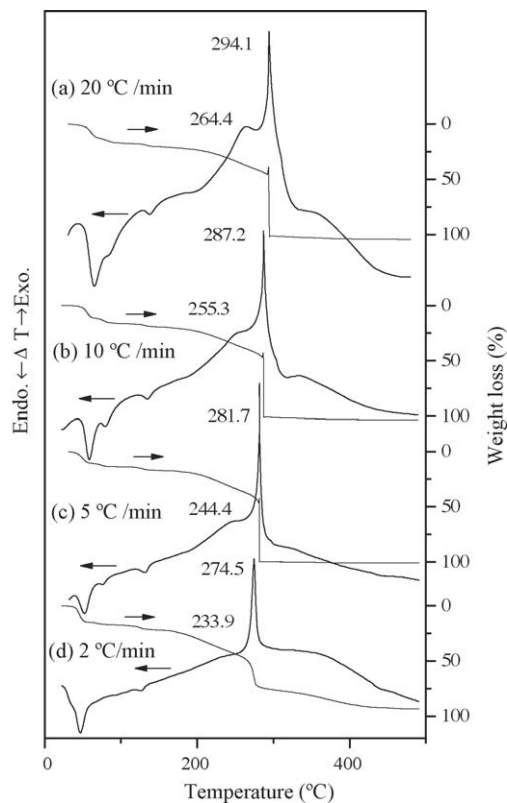


Fig. 8. DTA–TG curves of FePic at various heating rates.

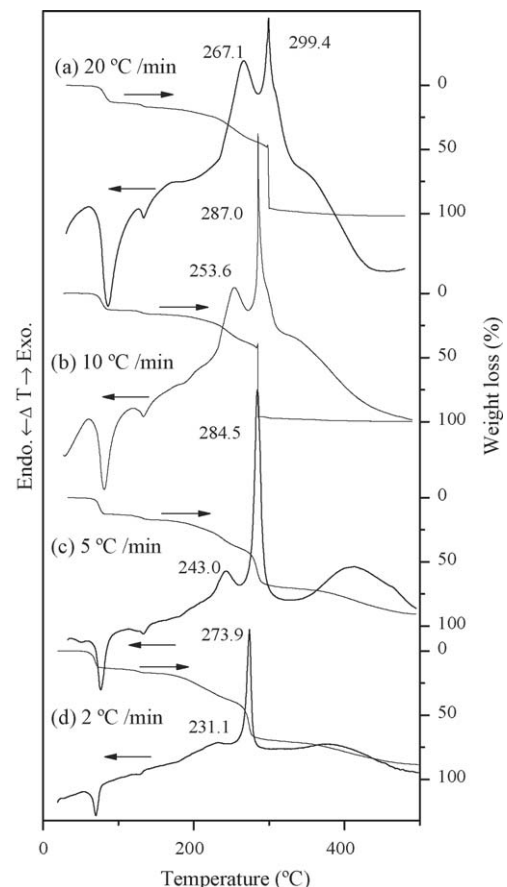


Fig. 9. DTA–TG curves of FePic(Ba) at various heating rates.

Table 1
Activated energy of decomposition

Salt	Peak temperature at 10 °C min ⁻¹ (°C)	Heating rate (°C min ⁻¹)	1/T (×10 ³)	K (min ⁻¹)	ln A (min ⁻¹)	E (kJ mol ⁻¹)
FePic	287.2	2	1.828	0.259	64.06	128.9
		5	1.802	0.600		
		10	1.785	1.133		
		20	1.763	2.458		
	255.3	2	1.972	0.166	35.9	69.1
		5	1.932	0.362		
		10	1.892	0.765		
		20	1.860	1.423		
FePic(Ba)	287.0	2	1.828	0.205	49.1	100.1
		5	1.793	0.535		
		10	1.775	0.873		
		20	1.747	1.942		
	253.6	2	1.983	0.147	30.7	59.3
		5	1.937	0.308		
		10	1.899	0.591		
		20	1.851	1.276		

of the exothermic peak into two peaks, at 255 and at 287 °C, indicating the maximum temperature of the peak. The first peak enlarges gradually and its weight loss increases. It appears that an increase in heating rate leads to difficulties in dehydrating FePic(Ba) to form the anhydrous salt. In particular, a salt with a small number of water molecules of crystallization does not necessarily show high thermal reactivity when subjected to a large heating rate.

Based on this method, Table 1 lists the evaluated activation energies divided into two peaks. As shown in Fig. 10, the ASTM plots show good linearity between the two peaks, although the ASTM method has been applied to a single reaction [7,8].

Although the value obtained is not absolute and changes according to the measurement conditions, there is a slight difference in thermal behavior in the case of hydrates with eight or more water molecules of crystallization. Based on the obtained values for heating rate dependence, it was thought that hydrated iron picrates would start to decompose before dehydrating to the anhydrous salt when the reaction progress rapidly. The investigation of the burning characteristics of these salts will be described elsewhere.

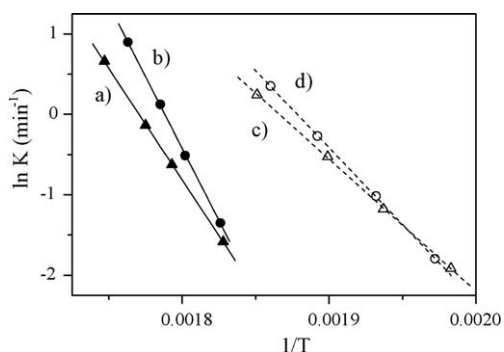


Fig. 10. ASTM plots of iron picrate. (a) FePic(Ba), (b) FePic, (c) FePic(Ba), (d) FePic.

4. Conclusion

Iron picrate was synthesized under conditions similar to those that result in the natural deterioration of chemical weapons. The following information was obtained by comparing salts obtained by different synthesis methods.

Iron picrate obtained by the iron corrosion reaction (FePic) has a large number of water molecules of crystallization compared to iron picrate octahydrate, which was obtained by the chemical synthesis method (FePic(Ba)). In addition, the FePic salt was found to be a mixture of hydrates whose composition varied according to the conditions under which crystal deposition occurred. Both salts have low sensitivity to friction and were found to be suitable for analysis by drop hammer testing, as they contain a large number of water molecules of crystallization.

Both salts started to decompose exothermally at 171 °C after exhibiting some endothermic peaks caused by dehydration. Under the experimental conditions of the thermal analysis, the iron picrates began to decompose before dehydration to the anhydrous salt occurred. However, the presence of an exothermic peak indicates that the anhydrous salt may have been partially formed during the decomposition.

As the heating rate increases, decomposition reactions prior to dehydration of the salt were inferred to be significant in the octahydrated iron picrate, FePic(Ba). Iron picrate with a small number of water molecules of crystallization may not necessarily show high thermal reactivity when subjected to a large heating rate. Based on the observed heating rate dependence, it is thought that under rapid reaction conditions the hydrated iron picrate should start to decompose before dehydration to the anhydrous salt occurs.

Holding tests were carried out under various drying environments. Although the water molecules were gradually released from FePic under certain conditions, it proved difficult to cause dehydration to the dangerous anhydrous salt by holding the sample for a long time in conditions similar to those found in the

natural environment. Formation of the anhydrous salt was not confirmed in this study.

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