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# The thermal behavior of potassium dinitramide. Part 1. Thermal stability

Ming Lei[*], Zhi-Zhong Zhang, Yang-Hui Kong, Zi-Ru Liu, Chun-Hua Zhu, Ying-Hui Shao, Pei Zhang

*Xi'an Modern Chemistry Research Institute, PO Box 18, Xi'an 710065, China*

## Abstract

In this paper, thermal analysis, X-ray photoelectric spectroscopy (XPS), etc. were used to investigate the thermal stability of potassium dinitramide (KDN). It was found that the thermal decomposition of KDN crystal conformed to the topochemistry. The decomposition product, $KNO_3$, formed eutectic system with KDN and decreased the liquefaction temperature of KDN. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Potassium dinitramide; Thermal stability

## 1. Introduction

Potassium dinitramide (KDN) is a new type of high energetic oxidizer of great interest for halogen-free, high-performance solid propellants. It can be used to replace AP or AN completely or partly. In recent year, KDN attracted the attention for more stable than ammonium dinitramide (ADN) and its phase-stabilization to AN [1]. A great deal of the investigation into synthesis and performance of KDN have been carried out by Russian researchers. In addition, thermal decomposition of KDN in solid and liquid state have been studied preliminarily [2,3]. They found an abnormal phenomenon that liquid KDN is more stable than solid state [3]. Furthermore, the US researchers investigated the geometry of $N(NO_2)_2^-$ in solid state and in solution [4]. However, further investigation on thermal behavior of KDN should be done.

In this paper, DSC, TGA and XPS technology were applied to investigate the KDN topochemistry of thermal decomposition in solid state and the influences on the thermal stability of KDN.

## 2. Experimental

### 2.1. Sample

KDN [$KN(NO_2)_2$], pale yellow crystal, was purified in water–methane alcohol. The sample was synthesized by Xi'an Modern Chemistry Institute.

### 2.2. Apparatus

The thermal analysis were carried out on a differential scanning calorimeter, Perkin-Elmer model DSC-2C and TA model DSC 2910, and a thermogravimetric analyzer, TA model TGA 2950, with sample mass of about 2–4 mg, and Al cell. The measurements were preformed in a dynamic atmosphere of nitrogen with a flow rate of 40 ml min$^{-1}$.

*Corresponding author.

In addition, an X-ray photoelectric spectroscopy (XPS) apparatus, model PE PHI-5400, with Mg target and in $3 \times 10^{-3}$ Pa vacuum, was used to study the chemical state of solid KDN sample on surface.

## 3. Results and discussion

### 3.1. Thermal stability of solid KDN

#### 3.1.1. Thermal character on DSC and TGA

The curve in Fig. 1(a) shows that the DSC of KDN is complicated. There is an exothermic peak and three endothermic peaks before 135°C; two main exothermic peaks between 228°C and 238°C and a set of endothermic peaks at last. The first three endothermic peaks are the phase transition peak of $KNO_3$ at 108.3°C, eutectic peak of KDN/$KNO_3$ system at 110.3°C and liquefaction peak of KDN at 128.0°C, respectively. If the sample contained less $KNO_3$, and

moreover less decomposition occurred in solid state, the endothermic peaks at 108.3°C and 110.3°C would be insignificant, only a fusion peak of KDN could be seen (see Fig. 1(b)). Thus the fusion peak temperature of the sample is the real melting point of KDN. It is 132°C when the heating rate was 10°C min$^{-1}$.

IR and TG analyses (in next part) indicate that $KNO_3$ and $KNO_2$ are the main products of decomposition of KDN in solid state. It is seen that a phase transition peak at 132.2°C and a fusion peak at 335°C appear on the DSC for $KNO_3$ (Fig. 1(c)), but only one fusion peak at 428.1°C for $KNO_2$ (Fig. 1(d)). By comparison, the DSC of decomposition remainder of KDN (Fig. 1(e)) is similar to curve C. Merely, the first endothermic peak is at 106.7°C, but the second endothermic peak is still at 342.5°C. From Fig. 1(f), we can see an eutectic peak existing in $KNO_3$/$KNO_2$ binary system. The eutectic temperature is 312.5°C. So we believe that the last sets of endothermic peaks on the DSC curve of KDN are those of fusion and liquefaction of $KNO_3$/$KNO_2$ binary system. For the eutectic peak, formed by a few residues, is very weak, it is often overlapped with liquefaction peak. So more often, only liquefaction peak of $KNO_2$ can be seen. It changes with the proportion of $KNO_3$ to $KNO_2$.

The endothermic peak at 108°C is the phase transition peak of $KNO_3$ which is formed by early decomposition of KDN (including that formed at room temperature during storage time). It could be proved by the endothermic peak at 106.7°C on DSC curve (Fig. 1(d)) of decomposition residue. Fig. 1(c) curve shows the phase transition temperature of $KNO_3$ formed by KDN is decreased, or changed by the effect of other decomposition product as $KNO_2$. The first two sharp endothermic peaks in Fig. 1(f) could prove it. In addition to a normal phase transition peak there is an endothermic peak at 118.1°C on DSC curve of $KNO_3$/$KNO_2$.

The two exothermic peaks between 228°C and 238°C are those of decomposition of KDN in liquid state.

While, the TG-DTG curves of KDN are relatively simple (Fig. 2). Besides a very slight mass loss (about 1.5%) at 120°C, the main process of mass loss occurs at 214.8°C, added up to about 35.6%, just between 30.3%, the mass loss of forming $KNO_3$ completely and 41.4%, that of $KNO_2$ completely.
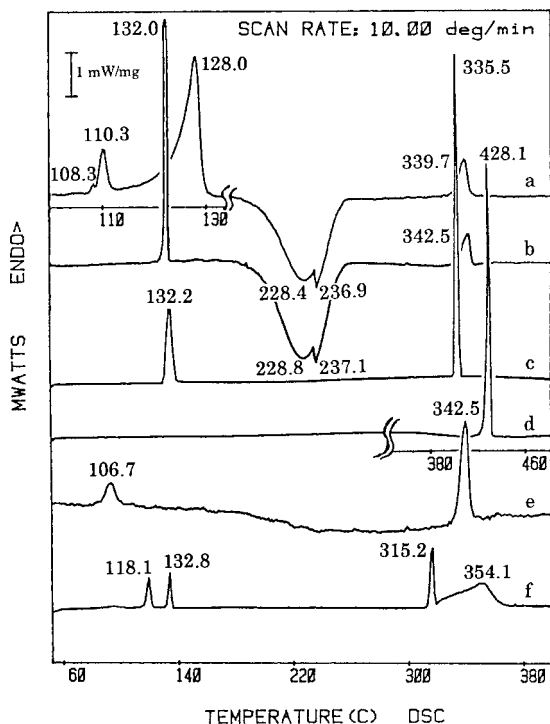


Fig. 1. The DSC curves of KDN, KDN/$KNO_3$, $KNO_3$ and $KNO_2$: (a) KDN; (b) pure KDN; (c) $KNO_3$; (d) $KNO_2$; (e) decomposition residue of KDN; (f) $KNO_3$/$KNO_2$ = 1 : 1.
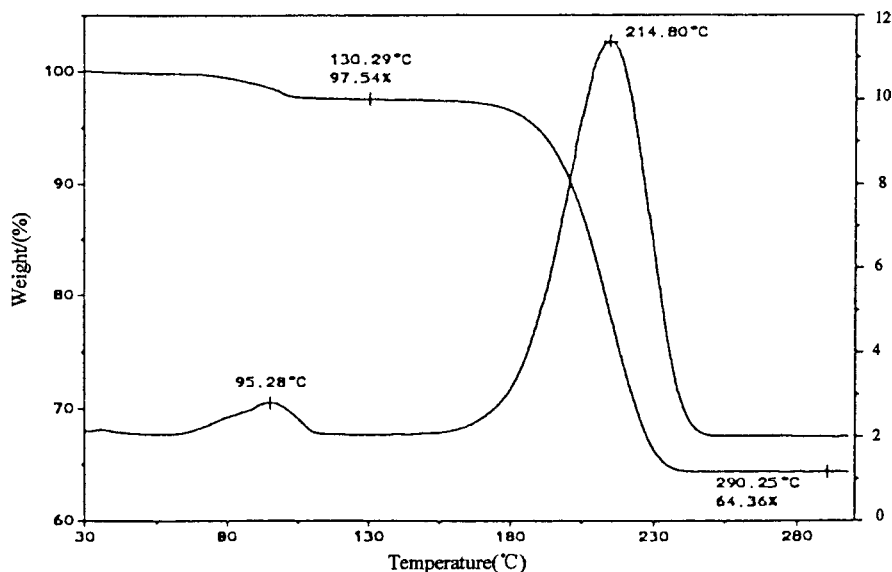
Fig. 2. The TG-DTG curves of KDN (model TA TGA 2950).

### 3.1.2. The influence of main factors on the thermal stability of KDN

3.1.2.1. Storage time and pretreatment of the sample. Fig. 3 and Table 1 show that same samples have various DSC curves for various storage time and pretreatment. Samples A1, A2 and B1–B4 were all purified in water–methane alcohol and stored dry. Comparison of the DSC curve of A2 with that of A1 shows: as the storage time increases, the endothermic peak at 109.1°C (eutectic peak of KDN/KNO$_3$) is drastically strengthened for A2, the

temperature of liquefaction peak, which is close to the melting point of KDN for A1, is decreased apparently to 128.7°C and a quite strong exothermic peak appears before liquefaction of A2, indicating an apparent decomposition in solid state.

Comparing B2, B3 and B4 with B1 shows: the first endothermic peak is apparently strengthened as the storage time increases, indicating the increase in the decomposition depth and in the product. But the peak in the second endothermic peak (i.e. the liquefaction peak of KDN) gradually reduces and the liquefaction temperature decreases from 124.5°C to 118.3°C, even

Table 1
The DSC data of KDN during various storage time and pretreatment

| Sample | Date of synthesis | Dry condition | Date of testing | Eutectic temperature (°C) | Liquefaction peak temperature (°C) |
|--------|-------------------|---------------|-----------------|---------------------------|------------------------------------|
| A1 | 12.12 | [a] | 12.24 | 109.1 | 131.7 |
| A2 | 6.17 | – | 12.25 | 110.8 | 128.7 |
| B1 | 8.28 | – | 9.1am. | 109.7 | 124.5 |
| B2 | 8.28 | – | 9.2am. | 109.7 | 123.8 |
| B3 | 8.28 | – | 9.4 | 110.1 | 121.0 |
| B4 | 8.28 | – | 9.18 | 110.7 | 118.3 |
| C1 | 9.4 | – | 9.10 | 110.4 | 126.1 |
| C2 | 9.10 | [b] | 9.10 | 110.9 | 121.1 |

[a] In dryer at room temperature.
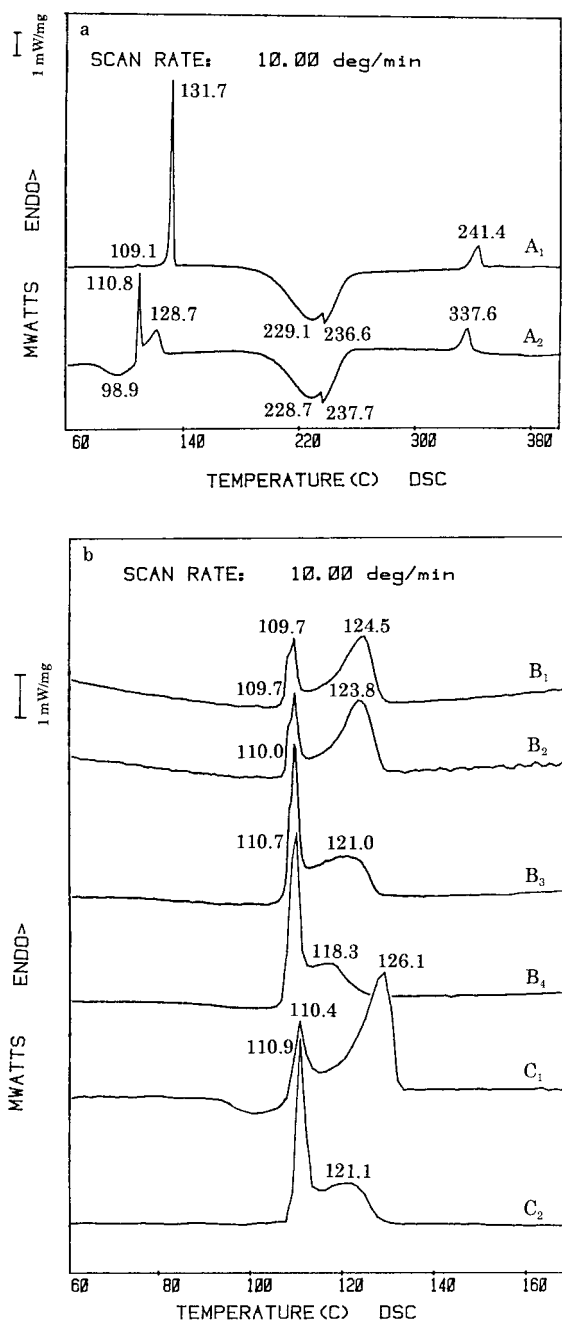[b] Dried at 85°C in vacuum for 2.5 h.

Fig. 3. The DSC curves of KDN sample during various storage time and pretreatment.

when there is a difference, just 4–5 h interval, of storage time between sample B1 and B2. Thus it is believed that the samples decomposed in part to form

$KNO_3$ in dry condition and room temperature. Therefore, an eutectic peak of KDN/$KNO_3$ appears in the DSC curve (including phase transition of $KNO_3$), the peak of which increases as the storage time and the decomposition depth of KDN increases. But the peak of liquefaction peak of KDN reduces with the increase in storage time, and relative surplus of KDN reduces, and its liquefaction temperature gradually approaches eutectic.

For various dry conditions, the fusion and the liquefaction processes of solid state of sample C1 is different from sample C2, obviously, the decomposition process giving $KNO_3$ is accelerated by vacuum dry condition at 85°C, with the eutectic peak strengthened, liquefaction peak weakened, and the peak temperature also decreased. So vacuum dry condition would do harm to the stability of KDN.

As the data of sample A1 and A2 show, although the thermal stability and the change in solid–liquid state are strongly affected by storage time, the decomposition of KDN in liquid state is affected slightly.

*3.1.2.2. Particle size.* It is seen from Fig. 4 and Table 2 that for the ground sample, the heat of the exothermic peak before fusion (or liquefaction) decreases significantly, as is also the mass loss. So the decomposition process of KDN is strongly affected by the particle state. The samples with large particle size, with many edges, or imperfect crystal, are liable to decompose and their thermal stability is poor, the reverse is stable.

Although the decomposition peak of the ground sample D2 reduces, i.e. the decomposition product $KNO_3$ reduces, the eutectic peak of KDN/$KNO_3$ strengthened and the liquefaction temperature of KDN decreased, the reason being the presence of $KNO_3$ partially formed in storage time. The DSC curve of the sample D1, which was tested immediately after grind, was different from that of the sample D2, which was stored for some time after grind. From this, it can be concluded that the decomposition of KDN took place at room temperature, especially in dry environment.

The sample D3 is solid, formed by cooling the liquefied sample. Although this sample underwent the decomposition in solid state before liquefaction, its behavior was similar to that of ground sample for it changed to fine crystal by drastically cooling. When
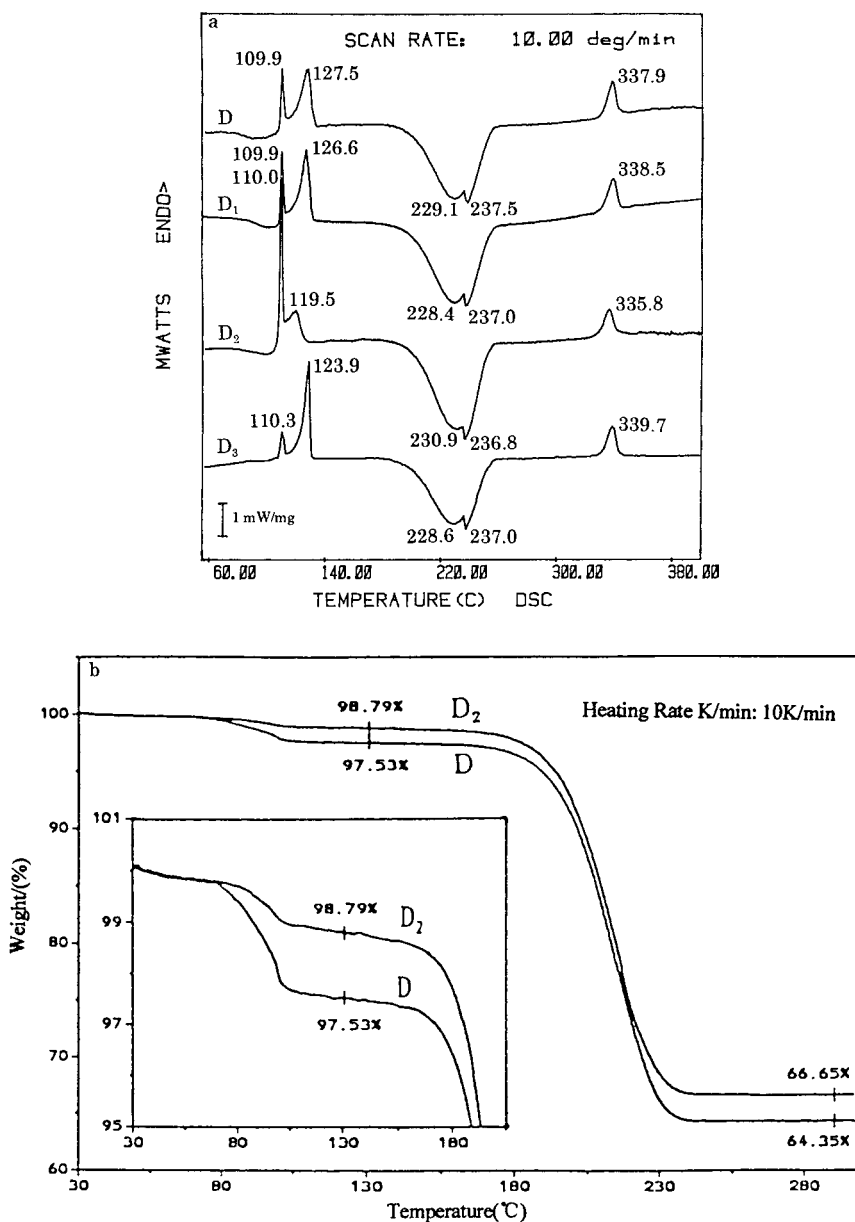
Fig. 4. The DSC and TGA curves of KDN in various crystalline state.

heated again, the exothermic peak of decomposition in solid state disappeared, and the eutectic peak reduced. The results show that its thermal stability improved. So the fine crystal is more stable.

*3.1.2.3. Moisture content.* The curves in Fig. 5 and the data of Table 3 show that the KDN containing certain moisture tends towards stability with less decomposition in solid state. Once the sample was dried, it would be decomposed significantly. Sample E2 was prepared by storing sample E1 in dryer for two days, while sample E3 was prepared by storing sample E2 in saturated solution of 35% relative humidity for five days, with 3.2% moisture content. Therefore,

Table 2
The data of DSC and TG of KDN in various particles state

| Sample | Particle state | Date of preparation | Date of grind | Date of testing | $\Delta H^a$ (J/g) | Mass loss[b] (%) | Eutectic temperature (°C) | Liquefaction temperature (°C) |
|--------|---------------|--------------------|---------------|-----------------|-------------------|------------------|---------------------------|-------------------------------|
| D | Large particle | 2.25 | – | 6.3 | 22.2 | 2.5 | 109.9 | 127.5 |
| D1 | Ground | 2.25 | 6.3 | 6.3 | 13.8 | – | 109.9 | 126.6 |
| D2 | Ground | 2.25 | 5.27 | 6.1 | 17.6 | 1.2 | 110.0 | 119.5 |
| D3[c] | Liquefied | 2.25 | – | 5.26 | 0.0 | – | 110.3 | 123.9 |

[a,b] They are the exothermic enthalpy and mass loss of decomposition in solid state, respectively.
[c] Sample D3 was prepared by drastically cooling after heating the sample D to 140°C.

Table 3
The influence of moisture content on KDN

| Sample | Moisture content (wt%) | $\Delta H^a$ (J g$^{-1}$) | Eutectic temperature (°C) | Liquefaction temperature (°C) |
|--------|------------------------|---------------------------|---------------------------|-------------------------------|
| E1 | Certain | 4.9 | 109.7 | 130.2 |
| E2 | 0 | 75.6 | 109.9 | 117.6 |
| E3 | 3.2 | 10.1 | 110.8 | 126.4 |

[a] It is the exothermic enthalpy of decomposition in solid state.

when the sample absorbed certain moisture again, the decomposition in solid state would decrease, so did the eutectic peak. The sample tended to be stable again.

## 3.2. Topochemistry of decomposition of KDN in solid state

According to above test results, i.e. the stability of KDN crystal before liquefaction (or fusion) and the



Fig. 5. The influence of moisture content on DSC of KDN.

decomposition on DSC and TGA depended on particle size, moisture content, and storage time of the sample, it is considered that the decomposition of KDN crystal conforms to the law of topochemistry.

There are many defects and cracks in the KDN crystal of large size and with striking edges and corners on surface or with the imperfection, which forms more reaction center and decomposes quickly. Under the decomposition process, the solid product $KNO_3$ would be adhered to these reaction sites to extend the defects and cracks and to promote the increase in stress on the crystal. When the stress increased to a certain degree, the crystal cracked and formed little crystals with new surface. Then the reaction would be continued on the increased specific surface. When the product $KNO_3$ has covered the surface of little crystal completely, the active center would be restrained and the decomposition would be stopped completely or partly.

From the fine crystal or ground samples of KDN, whose surface would be completely covered by $KNO_3$ formed owing to its partial decomposition during long storage time at room temperature, the active center are eliminated and the crystals do not crack easily due to its little size. Thereby, the process of "topochemistry" not occurs easily for these samples and they have good thermal stability.
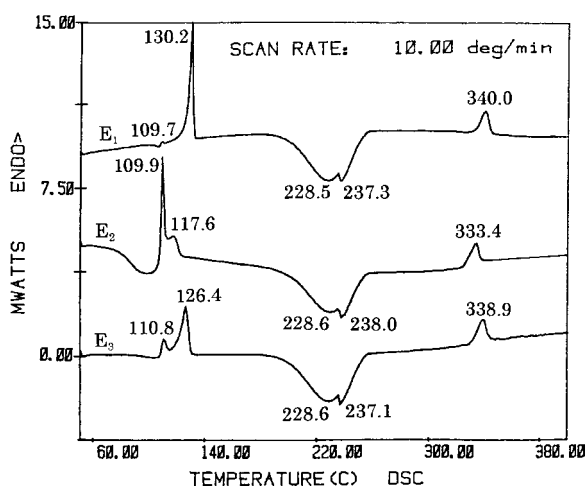
Similarly, the presence of a little of moisture is favorable to the elimination of the potential reaction center. Namely, certain moisture can stabilize the KDN crystal.

The decomposition in solid state and the process of liquefaction for KDN have been also observed by a microscope warming table. When temperature raised up to: 90°C, the crystal of sample D began to crack (the partial decomposition in solid state began); and to 97°C, the surface of the crystal began to darken (the product $KNO_3$ was formed and adhered to the surface). At 108°C, the crystal liquidated partly, and the liquid flowed bubbling up (the decomposition in liquid state continued); to 130°C, the liquefied sample became transparent (the liquefaction stopped, including eutectic formed by $KNO_3$) without increase in the bubble; and also to 150°C, was the same (the liquid KDN is stable relatively). After 160°C, the bubbles increased and enlarged with opaque substance formed (the decomposition in solid state began, $KNO_3$ and $KNO_2$ are formed). The preceding process of topochemistry can be proved by the observed phenomena, especially the decomposition in solid state.

In order to prove the above-mentioned facts that the decomposition of KDN in solid state was closely related to the coverage of $KNO_3$ on its surface, the chemical state of $K^+$ and the ratio of element K to N on surface of KDN were determined by means of X-ray photoelectron spectroscopy (XPS).

It is shown in Fig. 6 and Table 4, that for all samples except sample D1, the 2P electron binding energy of $K^+$ is in good agreement with that of $KNO_3$, indicating that the major $K^+$ on surface of these samples is in chemical state of $KNO_3$. When the
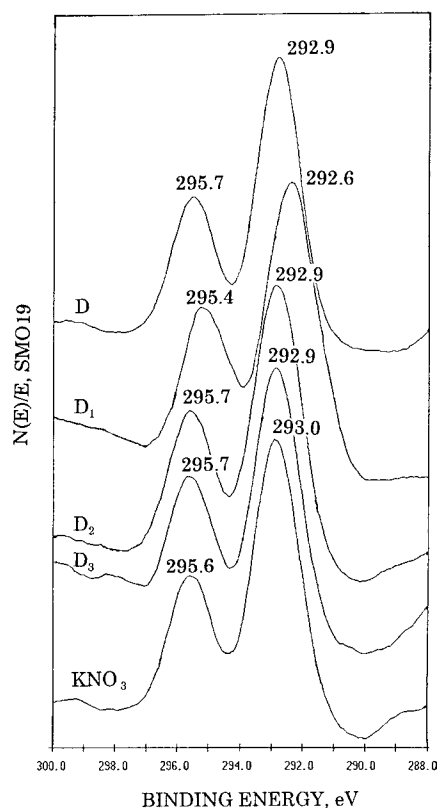


Fig. 6. Binding energy of $K^+$ in KDN.

sample is ground and new crystal surface has been formed, where the surface cannot be covered immediately by the decomposition product $KNO_3$, and the inner layer structure of KDN crystal can be emerged, the electron binding energy of $K^+/2P$ of D1 has been

Table 4
Electron binding energy of $K^+$ and K/N on surface for various crystal state

| Sample | Date of preparation | Date of treatment | Treatment | Date of testing | Electron binding energy of $K^+$ | | K/N |
|---|---|---|---|---|---|---|---|
| | | | | | $2P_{3/2}$ | $2P_{1/2}$ | |
| $KNO_3$ | – | – | – | 6.3 | 293.0 | 295.6 | |
| D | 2.25 | | Large cry | 6.3 | 292.9 | 295.7 | 0.47 |
| D1 | 2.25 | 6.3 | D ground | 6.3 | 292.6 | 295.4 | 0.40 |
| D2 | 2.25 | 5.27 | D ground | 6.3 | 292.9 | 295.7 | 0.55 |
| D3[a] | 2.25 | 6.2 | [b] | 6.3 | 292.9 | 295.7 | 0.41 |

[a] Sample D3 was prepared by drastic cooling after heating the sample D to 135°C.
[b] D after liquefaction.

decreased and is close to $K^+$ chemical state of KDN structure. When the ground sample has been stored for several days, where the new crystal surface has been covered by decomposition product $KNO_3$ again, the ionic state of $K^+$ on sample D2 crystal surface is as that of $KNO_3$ again. K/N value of crystal of all the four samples are greater than 0.33, the theoretical value of KDN. Thus it is seen that $KNO_3$ has been already accumulated on the crystal surface. Whereas, the specific surface of sample D2 is larger due to its being ground, so the K/N value is as high as 0.55. Since all the newly formed surface of D1 crystal has been not immediately covered by $KNO_3$, its K/N value is lowest, but is 0.40 still. Once the sample has been recrystallised by means of liquefaction, the $KNO_3$, which was originally accumulated on crystal surface, would be redistributed to new surface of fine crystal with larger specific surface, leading to the decrease of K/N value to 0.41.

It is shown from the results that the $KNO_3$ on KDN crystal surface formed by decomposition plays an important part in thermal behaviors of KDN, such as topochemistry of KDN in solid state, thermal stability, forming eutectic and liquefaction process, etc. Also, certain moisture content could stabilize KDN, for the polar molecular $H_2O$ is of benefit to eliminate the reaction center on crystal surface.

## 4. Conclusion

1. There is complicated thermal behavior from solid state to fusion in KDN. For KDN, the thermal stability, decomposition in solid state, formation of eutectic, and fusion or liquefaction process are dependent on particle size, storage environment and time and whether containing certain moisture, etc.
2. The decomposition of KDN in solid state conforms to topochemistry process. Cracking of large crystal would deepen the decomposition. The product $KNO_3$ or certain moisture covered on crystal surface would help to eliminate active center. They play the role as a stabilizer.

The liquefaction (or fusion) temperature of KDN is affected by quantity of $KNO_3$ product.

## References

[1] U.S. Patent 5 292 387.
[2] F.I. Dubovitskii et al., Dokl. Akad. Nauk 347 (1996) 763–765.
[3] F.I. Dubovitskii et al., Dokl. Akad. Nauk 348 (1996) 205 and 206.
[4] K.O. Christe, W.W. Wilson et al., Inorg. Chem. 35 (1996) 5068–5071.