The thermal behavior of potassium dinitramide
Part 2. Mechanism of thermal decomposition

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Abstract

In this paper, the thermal decomposition processes of KDN were investigated by means of thermal analysis and FT-IR with in situ cell. The results show that the decomposition of KDN in solid state is different from that of liquid state. The main condensed phase product of the decomposition in solid state is KNO_3. While the decomposition of liquid state form KNO_3 and KNO_2 simultaneously. The possible mechanism of the thermal decomposition in solid state has been proposed. A eutectic can be formed by product KNO_3 with KDN. The eutectic temperature of KNO_3/KDN system is about 109°C. Moreover another eutectic system can be formed by KNO_3 with KNO_2 to be eutectic temperature of about 315°C. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Mechanism of thermal decomposition; Eutectic system; Thermal analysis; In situ FT-IR

1. Introduction

Since potassium dinitramide (KDN) is a new type highly energetic oxidizer for solid propellants, the investigations on its thermal decomposition are of great importance. Dubovitskii et al. [1,2] investigated KDN thermal decomposition and proposed the mechanism of decomposition in its solid state and liquid state. Christe et al. [3] had also investigated the geometry of $N(NO_2)_2^-$ anion in solid and solution. These works are meaningful to investigation into stability and thermal decomposition of KDN.

In this work, based on Part 1, the mechanism of thermal decomposition of KDN was investigated by using a differential scanning calorimeter (DSC) and FT-IR with a heating in situ cell, which can in real time follow the process of the decomposition of KDN at heating. DSC found the eutectic systems and their temperatures for the process of decomposition.

2. Experimental

2.1. Sample

KDN, a pale yellow crystal, was synthesized by Xi'an Modern Chemistry Research Institute and was purified in methane alcohol–water.

2.2. Apparatus and experiment condition

The thermal analyses were carried out on a differential scanning calorimeter, model TA 2910, with sample mass of 2–4 mg. The measurements were
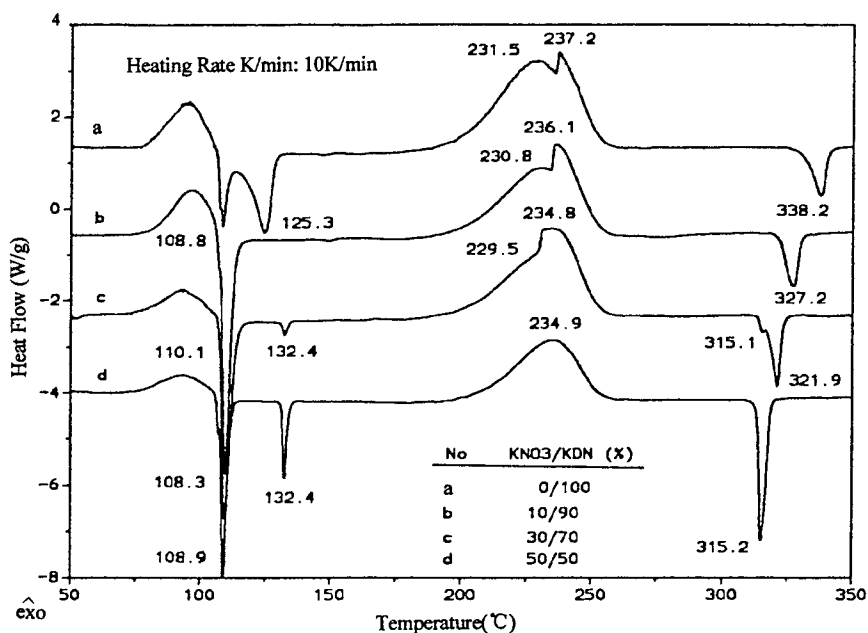
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Fig. 1. DSC curves of KNO_3/KDN system.

performed in a dynamic atmosphere of nitrogen with a flow rate of 40.0 ml min^{-1} and at heating rate of 10°C min^{-1}.

In addition, a Nicolet 60 SXR FT-IR spectrometer was used to follow the process of thermal decomposition of KDN in real time, with scanning 18 pieces IR spectra per min. The in situ cell, which used to follow the process of decomposition, was heated at about 20°C min^{-1}, and sample were tabletted with KBr.

3. Results and discussion

3.1. The eutectic system formed by KDN and its decomposition product KNO_3

As known in the first part of this paper [4] there is a set of endothermic peaks on all the DSC curves of KDN before 140°C. The temperature of an endothermic peak at 108–110°C do not changes, while its strength (endothermic enthalpy) changes with the quantity of decomposition product. But the temperature and endothermic enthalpy of another endothermic peak, immediately following above mentioned peak, reduces with the quantity of KNO_3 increases. The

shape and its change of the two endothermic peaks represent the characteristics of fusion and liquefaction process of typical binary eutectic system on DSC curve. It is shown that a binary eutectic system was formed by KDN with its decomposition product.

It is believed that the binary eutectic system consists of KDN and KNO_3 due to the formation of KNO_3 as main condensed phase product in decomposition of KDN in solid state (in following discussion). Moreover, no peak of the phase transition of KNO_3 at 132°C appears on DSC owing to the excess of KDN.

In order to prove the existence of the above-mentioned binary system, the DSC tests a set of samples, which were obtained by means of the mixing KNO_3 to KDN in various ratios, were performed and the curves were obtained, as shown in Fig. 1. From Fig. 1, it is shown that only enthalpy of the first endothermic peak has been increased owing to adding KNO_3, but its peak temperature has not been changed on the whole. While the endothermic enthalpy has been attained to maximum of 109.5 J/g in KNO_3/KDN = 10/90 wt% (see Table 1) and only an endothermic peak appears here (b curve). On adding KNO_3 to 30 wt%, the enthalpy of the peak has been decreased again and another endothermic peak appears at 132.4°C. This

Table 1
Influence of adding KNO_3 on thermal behavior of KDN

Sample	KNO_3/ KDN wt%	KNO_3/KDN system			KNO_3 phase transition T_c	KNO_3/KNO system			Decomposition in liquid state	
		T_e	ΔH_e	T_1		T_e'	$\Delta H_e + \Delta H_1'$	T_1'	T_{m1}	T_{m2}
a	0/100	108.8	42.8	125.3			43.7	338.2	231.5	237.2
b	10/90	110.1	109.5				40.9	327.2	230.8	236.1
c	30/70	108.3	105.8		132.4	315.1	42.3	321.9	229.5	234.8
d	50/50	108.9	61.9		132.4	315.2	62.5			234.9

T_e, T_e', T_1, T_1' (in °C) are eutectic and liquefaction temperatures of excess components for KNO_3/KDN and KNO_3/KNO_2 binary systems, respectively.
ΔH_e and $\Delta H_e'$ (in J g^{-1}) are the fusion enthalpy of eutectic of the two systems, respectively. $\Delta H_1'$ (in J g^{-1}) is the liquefaction enthalpy of KNO_3/KNO_2 system.
T_{m1} and T_{m2} (in °C) are the temperatures of two exothermic peaks of decomposition of KDN in liquid state, respectively.

peak would be large when more KNO_3 was added, but the peak temperature did not change, indicating that it is the phase transition peak of KNO_3 and that KNO_3 is already excess. For the fusion peak of KNO_3 is at 335°C far away, the liquefaction peak of KNO_3 cannot be seen. The results prove further that product KNO_3 of the decomposition of KDN can form binary eutectic system with KDN and its eutectic temperature is 108–110°C and the value has also been reported in the literature [2].

3.2. The eutectic system formed by decomposition products KNO_3 and KNO_2

There is a set of endothermic peaks at last part of DSC curve of KDN. Based on temperature these peaks are neither attributed to fusion of KNO_3 (375.5°C), nor that of KNO_2 (428.1°C). IR analyses (see following) show that the final solid products of decomposition of KDN are KNO_3 and KNO_2. The DSC curves of KNO_3/ KNO_2 system (see Fig. 2f in Part 1 of this paper) are those of a typical binary system with eutectic temperature at 315.2°C.

No eutectic peak appears distinctly in all DSC curves of KDN, the reason being a few of the decomposition products formed, in comparison to sample itself, and being that the content of KNO_3 in the eutectic binary system should be more than 70–80 wt%. So when KNO_3 was added up to 30 wt%, the eutectic peak of KNO_3/KNO_2 could be distinguished from this set of endothermic peak (curve c in Fig. 1). Only a fusion peak of eutectic could be seen at 312.5°C when KNO_3 was added up to 50 wt% (curve d

in Fig. 1). Therefore, it is considered that the last endothermic peak on the DSC of KDN is attributed to the liquefaction of KNO_2 of KNO_3/KNO_2 binary system.

It is deserved attention that the different temperatures of liquefaction peak of KNO_2 have been found from all DSC curves of various KDN samples in Part 1 of this paper. When solid KDN decomposed more deeply or fusion peak of KNO_3/KNO_2 was stronger, the liquefaction peak temperature was also lower. So, KNO_3 is considered to be the main solid product of decomposition of KDN in solid state.

3.3. Mechanism of thermal decomposition of KDN

The partial IR spectra obtained from following the decomposition process of KDN by a heating in situ cell are shown in Fig. 2. It is obviously found from Fig. 2 that the processes of disappearance of the absorption bands of N–nitro group (N–NO_2) (1530, 1431, 1344 and 1178 cm^{-1}) and N–N (1023 cm^{-1}) and those of the increase in strength of the bands of –NO_3 (1384 cm^{-1}) –NO_2 (1249 cm^{-1}) could occur as increase in temperature. The IR spectra in Fig. 2 can be divided into four groups. In first group, from room temperature to 157.2°C (spectrum 1–4), N–NO_2 absorption band changes greatly and do not disappear, while –NO_3 absorption band at 1384 cm^{-1} is strengthened somewhat. In this temperature range the thermal behavior of KDN on DSC is corresponding to the processes of decomposition in solid state and of liquefaction. In second group from 157.2°C to 190.6°C (spectrum 4–7), changes in spectra are rela-
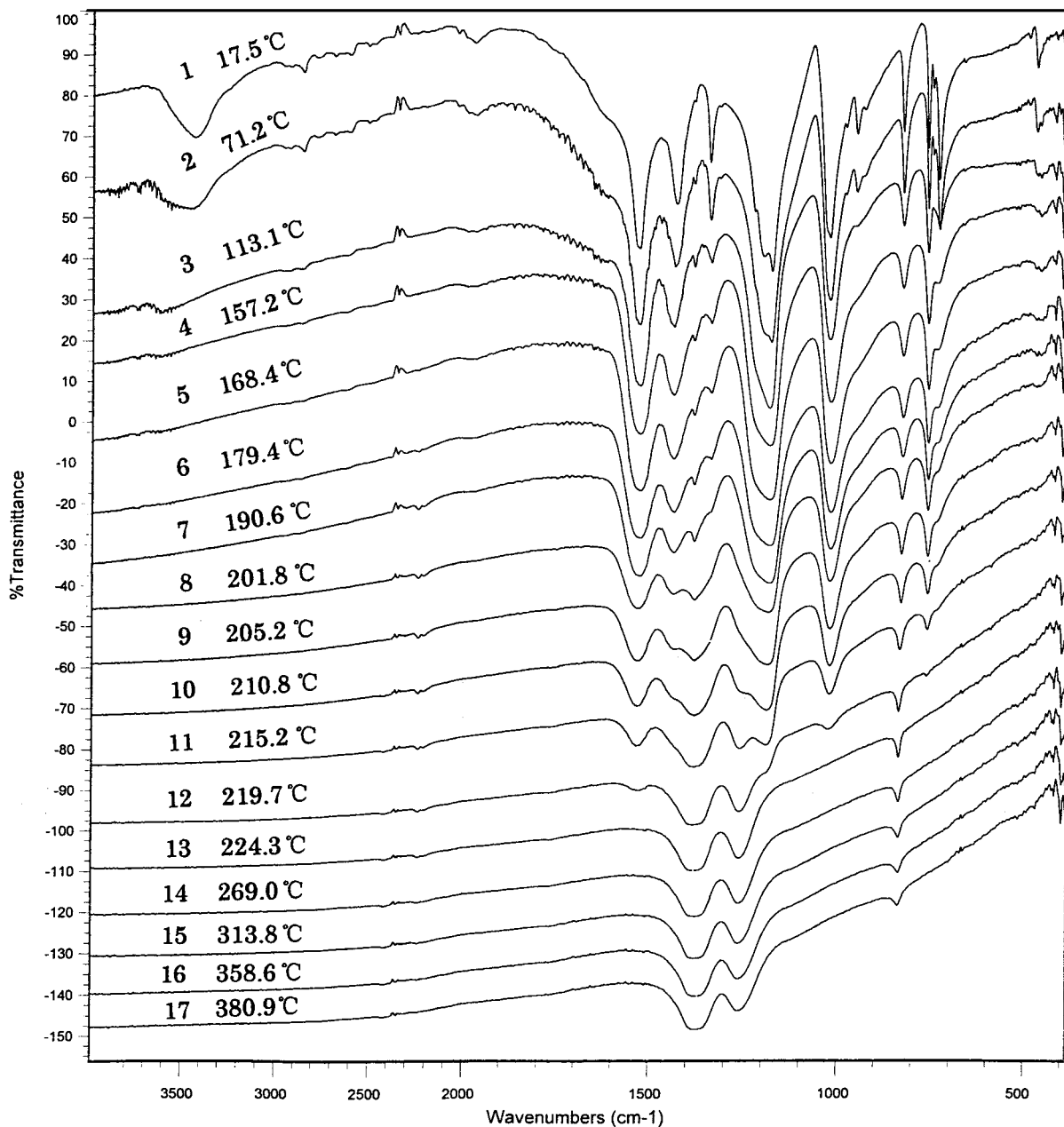
Fig. 2. The partial IR spectra for a heating in situ cell for following the decomposition process of KDN.

tively slight. This process is corresponding to relatively stable stage of liquid KDN on DSC. In third group from 190.6°C to 224.3°C (spectrum 7–13), all absorption bands of N–NO_2 and N–N weaken gradually to disappear, but the absorption bands of –NO_3 and –NO_2 strengthen gradually, which are to the decomposition stage of KDN in liquid state. In the fourth group from 224.3°C to 380.9°C (spectrum 13–17), the spectra change relatively slightly, only the relative quantity of –NO_3 to –NO_2 change (see next).

These processes are corresponding to the later stage and the end of decomposition of liquid KDN on DSC.

From the above analyses it is shown that KNO_3 is the main solid product of decomposition stage of KDN in solid state, also confirmed by the following facts. On DSC curve of KDN, the strength of eutectic peak of KNO_3/KDN and the change in temperature of liquefaction peak of KNO_2 of KNO_3/KNO_2 are in close relationship with the depth of solid decomposition. The strength of eutectic peak of KNO_3/KDN is increased with solid decomposition deepened. If the mechanism of solid decomposition was the same as liquid decomposition, namely the ratio of KNO_3 and KNO_2 formed in solid decomposition would be same as liquid, the liquefaction temperature of KNO_2 in KNO_3/KNO_2 system should not be changed in spite of the depth of the solid decomposition. The opposite results proved that the process of decomposition in solid state is different from that of liquid state and the liquefaction temperature of KNO_2 decreases as the depth of solid decomposition decreases.

On the basis of the analyses of the molecular structure difference between solid and liquid KDN in literature [2], it is believed the charge of $N(NO_2)_2^-$ anion in liquid phase is uniformly distributed and the anion has the plane structure with utmost stability. But in crystal state, the two nitro groups of the anion are spread and are not conjugate. The charge is precedently gathered on one nitro group, and the two N–N bonds are not identical. So the anion in crystal is easily decomposed to form N_2O and NO_3^-. From geometry of molecular crystal and data of IR and Raman spectra, Christe et al. [3] believed that the two nitro groups of KDN crystal are not in the same plane, their N–NO_2 bonds make an angle of $22.6°$ with each other and the bond lengths are not the same, to lead to that the –NO_2 groups are asymmetrical. On the basis of the above analyses, the following mechanism of decomposition of KDN in solid state is proposed:

$$KN(NO_2)_2 \rightarrow KNO_3 + N_2O$$
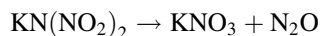
The data of high pressure DSC show [5] that the strength of the exothermic peak of decomposition in solid state and that of eutectic peak of KNO_3/KDN would be decreased by increasing pressure, indicating that the condition at high pressure is not favorable to the solid decomposition reaction which released gas. Therefore, it also supports the above-mentioned mechanism of releasing N_2O gas during decomposition process.

The DSC curves of KDN show that the two exothermic peaks can be found in the decomposition of liquid KDN and their temperature are $228–230°C$ and $236–238°C$, respectively. Between $230°C$ and $236°C$, there is an obvious peak valley. It possibly indicates that there are macroscopically at least two main stages in decomposition of KDN in liquid state.

The relationship curves of relative strength of characteristic absorption with temperature were obtained from integrating corresponding characteristic peak, which were obtained from the spectra of FT-IR with the heating in situ cell. The relationships of the characteristic peak strengths of N–NO_2, –NO_3, –NO_2 and N_2O in the decomposition process of KDN with temperature (time) are shown as Fig. 3. It is known from these results that a sudden change in the strengths of all characteristic peaks occurs from $224°C$ to $234°C$. It is indicated that N–NO_2 disappeared and –NO_3 got to maximum gradually. Then the latter basically kept constant strength with the temperature increased continuously. While –NO_2 and N_2O all got to maximum and then tended to decrease with temperature increased continuously. The IR absorption band of N_2O and its relative strength change with temperature is shown in Fig. 4 and Table 2.

According to the above-mentioned analyses, the possible mechanism of decomposition of KDN in liquid state is proposed as follows:

First stage (exothermic peaks on DSC at $228–230°C$):

Table 2
Strength of characteristic absorption peak of product N_2O at various temperatures

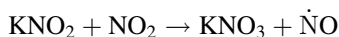| Temperature (°C)	135.1	157.2	168.2	179.4	190.6	212.9	224.3	269.0	313.8	358.6	380.9
Relative strength of N_2O absorption peak	0.0	0.0	0.15	0.49	1.33	3.97	4.77	3.65	2.68	1.93	1.22
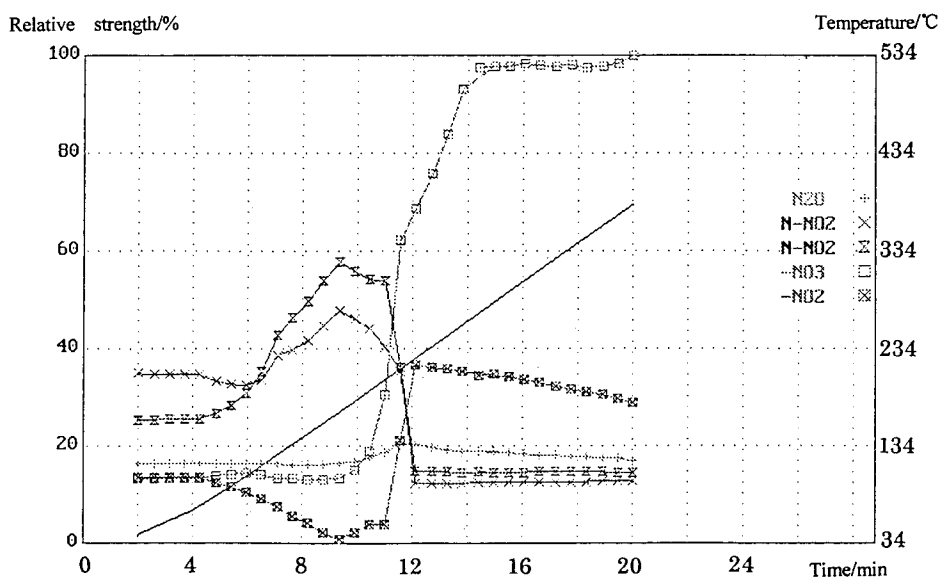
Fig. 3. Relationship curves of relative strength of IR characteristic peak with time and temperature.

$$KN(NO_2)_2 \rightarrow K\dot{N}(NO_2) + NO_2$$

$$K\dot{N}(NO_2) + NO_2 \rightarrow KNO(NO) + NO$$

$$2K\dot{N}(NO_2) \rightarrow 2KNO_2 + \dot{N}(NO_2)$$

$$KNO_2 + NO_2 \rightarrow KNO_3 + \dot{N}O$$
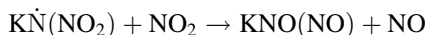
Second stage (exothermic peaks on DSC at 236–238°C):

$$\dot{N}(NO_2) \rightarrow [O] + N_2O$$

$$\dot{K}NO_2 + [O] \rightarrow KNO_3$$
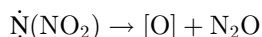
Dubovitskii et al. [1] studied the thermal decomposition of KDN in liquid state by labeled atom technology. He proposed that KDN firstly splits off a nitro group, forming NO_2, and the stoichiometric reaction equation is shown as follows:

$$KN(NO_2)_2 \rightarrow NO + 0.5\,N_2O + 0.5\,KNO_2$$
$$+0.5\,KNO_3.$$
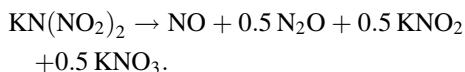
He also believed that the intermediate product, double free radical $\dot{N}NO_2$, has relative good stability and it may not be decomposed until relative high temperature. When $\dot{N}NO_2$ is decomposed at relatively high temperature to produce free [O], which has much stronger oxidizing property than that of NO_2, the stronger oxidizing reaction of [O] with

KNO_2 would occurred and KNO_3 would be produced. This moment, a stronger exothermic peak would overlap another exothermic peak on DSC. Thus the later exothermic peak (236–238°C) rose abruptly and KNO_2 reduced, while KNO_3 increased continuously (Fig. 3) and N_2O also increased to maximum at 224°C (Fig. 4 and Table 2).

Dubovitskii et al. [2] also discovered that the yield of N_2O is more at 220°C during the decomposition of KDN at constant temperature.

It can be seen from Fig. 1 that adding KNO_3 would cause the second exothermic peak of liquid decomposition to change, i.e. the temperature of the peak would be advanced and the strength of the peak would be strengthened. In addition, adding KNO_2 had similar results. It is possible for the reason that KNO_3 or KNO_2 has the ability to capture the double free radical $\dot{N}(NO_2)$ and hence the concentration of this intermediate product is increased. So the decomposition temperature can be decreased and the exothermic peak increased.

In addition, it is shown from the data of high-pressure DSC [5] that for the first exothermic peak of decomposition of KDN in liquid state its peak temperature is risen and strength is strengthened with pressure increase. The corresponding activation energy of the first exothermic peak is decreased.
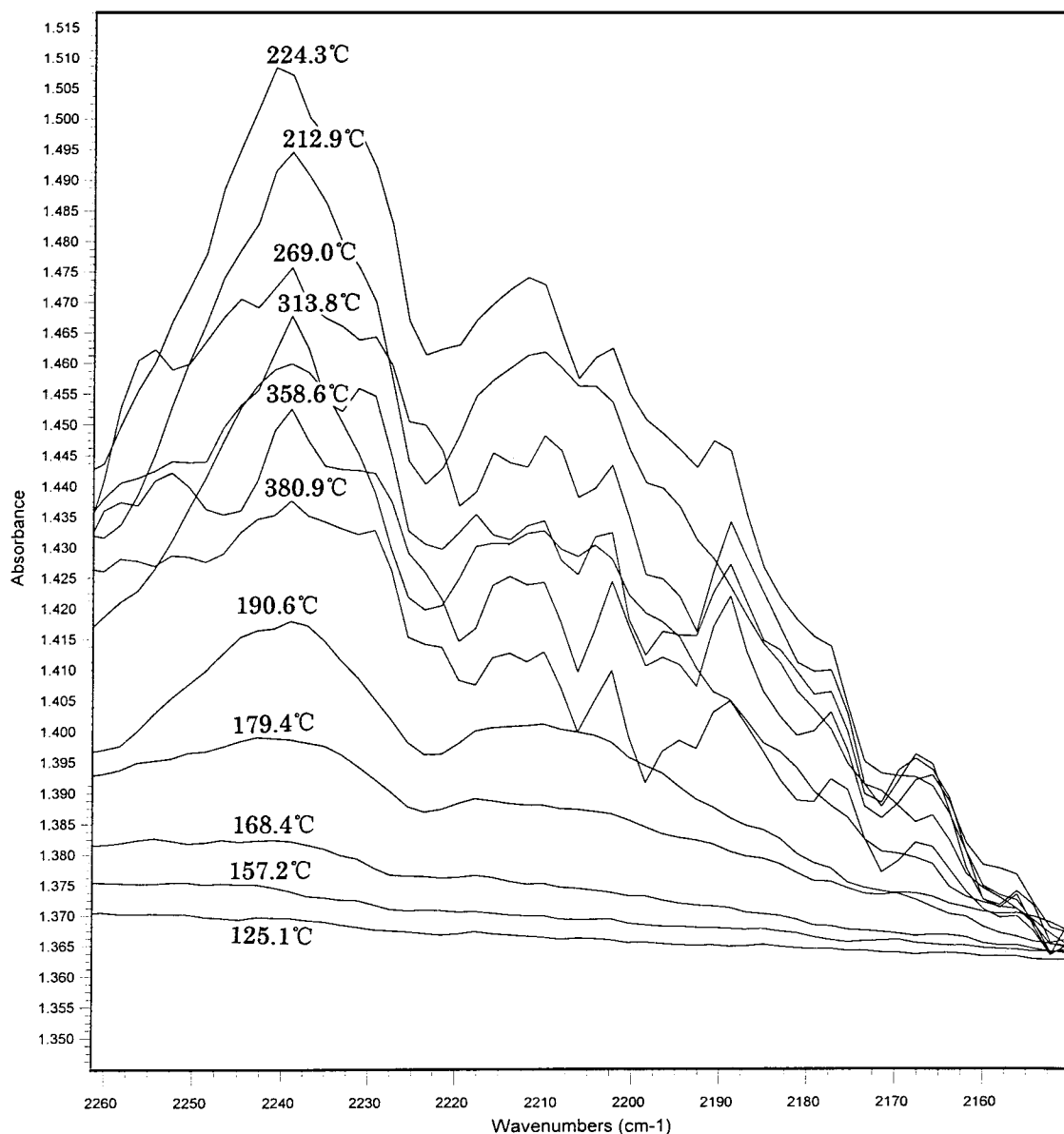
Fig. 4. Characteristic absorption peak of product N_2O at various temperatures.

But the second exothermic peak and its corresponding activation energy are not changed. Obviously, increasing pressure is favorable to increase the concentration of NO_2 with relative stronger oxidizing property in liquid state and to the second and the forth step process in the first stage of above decomposition mechanism. Therefore the first exothermic peak is advanced and strengthened. To second stage, the reaction system may be in solid state already and the free radical $\dot{N}(NO_2)$ may be captured on KNO_3 and KNO_2. So, the pressure influences the reaction process of the second stage very slightly.

Thus, it is clear that these results all support the above-mentioned decomposition mechanism of KDN in liquid state.

4. Conclusion

1. There are two binary eutectic systems in the decomposition process of KDN, One system consists of KDN and decomposition product KNO_3, with eutectic temperature at about $109°C$ and the other consists of the two products KNO_3 and KNO_2, with eutectic temperature at about $312.5°C$.
2. The main products of decomposition of KDN in solid state are KNO_3 and N_2O. While the decomposition in liquid state, besides KNO_3 and N_2O, KNO_2 and NO (or NO_2) are the main products. The decomposition in liquid is divided into two main stages.

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