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INVESTIGATION OF THE THERMAL STABILITY OF NITROGUANIDINE BELOW ITS MELTING POINT

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ABSTRACT

The thermal stability of several nitroguanidines (NQ) of various grain sizes at temperatures below their melting points has been investigated by means of thermal analytic techniques and the Bourdon manometic method. The melting points and the changes in the crystals near their melting points for these NQ were measured and observed. The results showed that the grain size is the main factor influencing the thermal stability of NQ: smaller crystals have a higher stability than larger ones, and their melting points are closer to the actual one. It has been attempted to interpret these results from the view point of "topochemistry" or "formation and growth of nuclei". Moreover, the kinetic parameters of the decomposition of the solid phase were determined and a mechanistic function of the decomposition process was found, with the aid of a computer, to be $x = k_1t^5$, i.e. the reaction rate of decomposition of NQ, $dx/dt = k_2t^4$, increases with the fourth power of time.

INTRODUCTION

The thermochemical behaviour of nitroguanidine (NQ) is of interest because of the unusual properties of its decomposition process. Since it was suggested that NQ has two different structures [1,2], early studies on its thermal behaviour were related to these structures. It is now certain that NQ has only one crystal structure of the orthorhombic crystal system. Therefore, it is necessary to reinvestigate the main factors which influence the thermal stability. Volk [3] presented the decomposition process after studying mass spectroscopic (MS) and isothermal weight loss data of NQ at a lower temperature and examined the effects of grain size on the thermal decomposition.

In previous papers, we have presented the course of the thermal decomposition of NQ and verified the initial step in the mechanism by using a quantum-chemical based calculation [4,5]. Although Pasman and Putte [2] were not exactly right in considering the existence of two structures having influence on the thermal stability of NQ, the decomposition process of the crystals observed by them was in agreement with the data obtained in our

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work. In the present work the main factors influencing the thermal stability of NQ have been investigated using analytical techniques.

EXPERIMENTAL

Materials

Three NQ samples of needle-like crystals were used: (a) crude product A (NQ-A) of 98.7% purity and grain size 2–15 μm; (b) recrystallized product N (NQ-N) of 99.2% purity and needles 100–300 μm in length was reduced by milling to two specimens to 30–50 and 2–15 μm; and (c) crude product B (NQ-B) of 98.8% purity and grain size 3–17 μm, was blended with a few additive and dispersing agents and the needles were reduced in size by milling.

Methods

The thermal analyses of the samples were performed on Perkin–Elmer DSC-2C and TGS-2 type instruments using a nitrogen atmosphere (flow rate 40 ml min^{-1}) and aluminium cells. The dependence of the evolved gases on time was obtained using the Bourdon manometric method in which samples are kept under vacuum with a loading density of 1×10^{-3} g cm^{-3}. The melting point of NQ was measured using a model FP51 melting point instrument. The changes occuring during heating of the compound were observed using a Microwarm Stage.

RESULTS AND DISCUSSION

Thermal stability of NQ

Results of DSC and TG analyses

The differential scanning calorimetry (DSC) curves of the three NQ samples and the curves for various grain sizes at a heating rate of 20 °C min^{-1} are shown in Fig. 1. The curve of coarse NQ-N shows a small and slow exothermic peak before the endothermic melting peak. After the grain size of NQ-N was reduced by milling, the exothermic peak progressively disappeared, the endothermic melting peak progressively sharpened, and the temperatures of the endothermic and exothermic peaks of the main decomposition step followed by melting also rose in succession, as shown in Table 1. Similar results were obtained for other heating rates of NQ-N and the same results were observed for NQ-A and NQ-B (see Fig. 1 and Table 1). The comparison between these results shows that the differences between

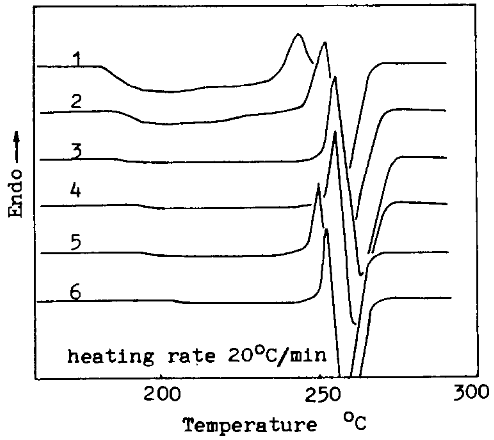

Fig. 1. DSC curves of various NQ samples. (1) NQ-N, 100–300 μm; (2) NQ-N, 30–50 μm; (3) NQ-N, 2–15 μm; (4) NQ-A, 2–15 μm; (5) NQ-B, 3–17 μm; (6) NQ-B, < 3 μm.

the results for various grain sizes are greater than the differences in the results for the crude and recrystallized products; these differences would be even greater if there was a large disparity in grain size. Even though an additive and a dispersing agent were put into NQ-B, no obvious exothermic peak appeared in its DSC curve before melting. The temperatures of both second exothermic peak and the endothermic melting peak were higher than those for the recrystallized product of coarse grain size. The reason for this is that NQ-B had a smaller grain size.

The melting point data were similar to those of the DSC curve (Table 2). Because of the difference in grain size, the difference in the melting points of the same crystalline products was as high as 7.3° C. However, there was no difference between the melting point of NQ-N and NQ-A the grain sizes of which were both in the range 2–15 μm. Owing to the presence of a few additive and dispersing agents in NQ-B, its melting point is lower.

The results obtained from above DSC curves were further confirmed by the TG–DTG curves. Figure 2 shows that the DTG curves are completely in

TABLE 1

DSC data (° C) of the NQ samples at a heating rate of 20 ° C $\min^{-1}$

	NQ samples					
	NQ-N			NQ-A	NQ-B	
Grain size (μm)	100–300	30–50	2–15	2–15	3–17	< 3
First exothermic peak	219.0	–	–	–	–	–
Second exothermic peak	249.6	259.4	263.3	263.7	256.2	259.9
Endothermic melting peak	243.8	252.9	256.4	256.3	251.2	252.9

TABLE 2

Melting points (°C) of the various NQ samples

	NQ samples					
	NQ-N			NQ-A	NQ-B	
Grain size (μm)	100–300	30–50	2–15	2–15	3–17	< 3
Melting point	232.8	237.3	240.1	240.0	236.1	236.0

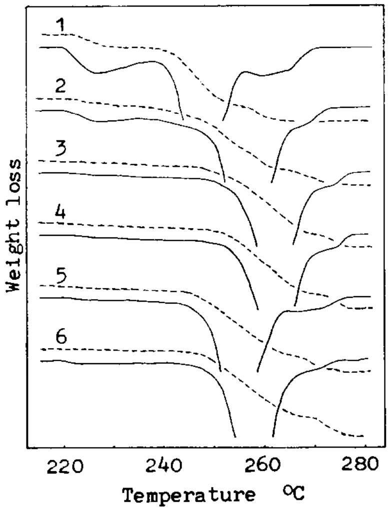

Fig. 2. TG (- - - - - -) and DTG (———) curves of the NQ samples at a heating rate of 20 °C min^{-1}. (1) NQ-N, 100–300 μm; (2) NQ-N, 30–50 μm; (3) NQ-N, 2–15 μm; (4) NQ-A, 2–15 μm; (5) NQ-B, 3–17 μm; (6) NQ-B, < 3 μm.

agreement with the DSC ones, indicating that the small and slow exothermic peak in DSC corresponds to the TG weight loss process. Obviously, there was a considerable amount of decomposition of the coarse NQ (up to 13.5%) before it melted. The percentage weight loss decreased progressively with the reduction in grain size. This decrease was only 1–2% in the case of a quite

TABLE 3

Weight loss (%) of the NQ samples over the heating range 50–220 °C during a TG run at a heating rate of 10 °C min^{-1}

	NQ samples					
	NQ-N			NQ-A	NQ-B	
Grain size (μm)	100–300	30–50	2–15	2–15	3–17	< 3
Melting point	13.5	4.1	1.0	1.7	3.4	2.1

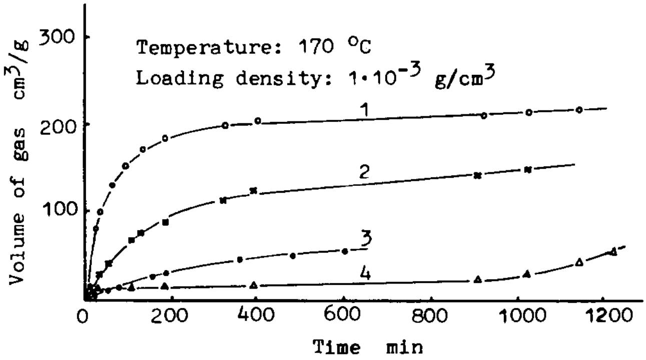

Fig. 3. Volume of gas evolved versus time for the NQ samples. (1) NQ-N, 100–300 μm; (2) NQ-N, 30–50 μm; (3) NQ-N, 2–15 μm; (4) NQ-A, 2–15 μm.

fine grain (Table 3). It was also shown that the differences in the thermal behaviour between the recrystallized and crude samples were far smaller than those due to the differences in grain size.

Results of the vacuum Bourdon manometric test

In order to further prove that the thermal stability of NQ depends mainly on its grain size, a vacuum Bourdon manometric test (VBMT) was performed at 170 °C. The curves of the volume of gas evolved versus time and the volume of gas evolved in two 5-h runs are shown in Fig. 3 and Table 4, respectively. The results in Fig. 3 and Table 4 again show the dependence of the thermal stability on the grain size; i.e. the coarser the grain the higher the volume of gas evolved from NQ decomposition during the first 5 h. However, after heating for 5 h the influence of grain size is not notable.

Decomposition process of NQ crystals

The results presented above show that there is considerable weight loss associated with the thermal decomposition before melting of the coarse NQ, which gradually decreases as the grain size is reduced. IR analysis of the sample near the end of this process (i.e. before melting) showed that the

TABLE 4

Volume of gas evolved (ml g^{-1}) for NQ samples measured using VBMT at 170 °C

	NQ samples			
	NQ-N			NQ-A
Grain size (μm)	100–300	30–50	2–15	2–15
First 5 h	200	110	40	15
Second 5 h	8	20	17	3

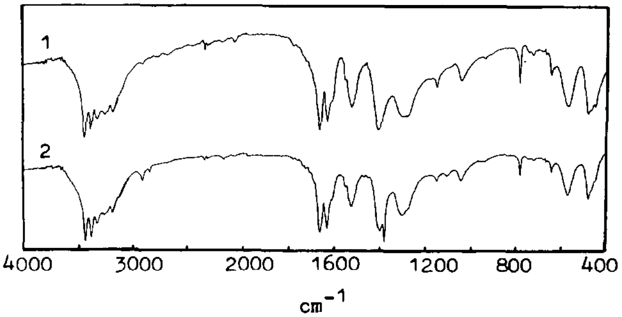

Fig. 4. IR spectra of NQ-N (100–300 μm) and its thermally treated sample. (1) Untreated NQ-N; (2) sample after weight loss (13.5%) during the TG run.

thermally treated NQ sample was not notably different from the untreated NQ (see Fig. 4).

In order to interpret this phenomenon, the thermal decomposition of coarse crystals (100–300 μm) was observed by means of a Microwarm Stage. The results showed that when the temperature reached 130 °C the needles and transparent crystals became milky white. As the temperature was increased to above 130 °C the crystals began to break down into very small grains. Finally, when the temperature was raised to the melting point, strong decomposition occurred. The same phenomenon was observed by Pasman and Putte [2] during heating tests in an open vessel.

We thought that this phenomenon could be explained by means of the theory of a "topochemical reaction" [6]. At the surface of the crystals there are small cracks or defects (i.e. crystal imperfections), which can form many potential reaction centres (nuclei). The decomposition begins at the centre of these defects (nucleus formation) and, consequently, more reaction centres are formed by a kind of chain process (nucleus growth). Moreover, owing to the accumulation of condensed-phase products, the crystals produce additional strains and hence further cracking occurs [7]. This process occurs repeatedly and causes part of the NQ to decompose and many small size crystals to be formed.

The solid product melamine, characterized by a high thermal stability, forms on the surface of small size crystals as a deactivator and fine NQ thereby loses activity and is prevented from decomposing. Volk [3] likened the effect of melamine to that of calcium azide coated with paraffin which thereby loses its activity [6]. Processes similar to that described above have also been described by Pasman and Putte [2]. When the temperature is raised to above the melting point the transformation from solid to liquid occurs, melamine loses its deactivation properties, and the decomposition reaction is accelerated greatly with increasing temperature causing a sharp exothermic decomposition. It is obvious that fine NQ crystals are less likely to crack because the strains acting on small size crystals are less during

TABLE 5

T_m of the first exothermic peak for NQ-N (100–300 μm) at various heating rates

ϕ (°C min^{-1})	2.50	5.00	10.00	20.00
T_m (°C)	180.0	190.5	204.2	219.0

heating. Therefore, at temperatures below the melting point fine NQ has a higher thermal stability than coarse NQ. In addition, because the quantity of fine NQ which decomposes before melting is less than for coarse NQ, the accumulation of the condensed-phase products on fine NQ is less than that of coarse NQ, which results in a rise in the melting point and the decomposition point. The above therefore accounts for the observed increase in melting points with a decrease in grain size.

Kinetics of decomposition of NQ crystals

The peak temperatures (T_m) of the first exothermic decomposition peaks in the DSC curves were obtained at various heating rates (ϕ) for a coarse NQ-N (100–300 μm) sample (Table 5). On the basis of the relation of $\ln \phi/T_m^2 - 1/T_m$ in Kissinger's equation [8]

$$\ln \phi/T_m^2 = \ln AR/E - E/RT_m \tag{1}$$

the activation energy E, the pre-exponential factor A and the correlation coefficient r were found by regression analysis to be 90.1 kJ mol^{-1}, 7.75 ($\log A$, s^{-1}) and 0.9983, respectively.

The percentage weight loss (Table 6) at various temperatures on the first peak of the DTG curve can also be used in kinetic calculations. According to the Coats–Redfern equation [9]

$$\ln g(x)/T^2 = \ln \frac{AR}{\phi E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \tag{2}$$

where x is the percentage weight loss, $g(x) = k_0 t$ is the kinetic mechanistic equation (k_0 is constant, t is time), R is the gas constant, T is the temperature (in K), and using 11 mechanistic functions (Table 7) [10], the

TABLE 6

The weight loss (%) of NQ-N (100–300 μm) from the TG curve recorded at a heating rate of 1°C min^{-1}

Temperature (°C)	160	165	166	167	168	169	170	171
Weight loss (%)	0.04	0.22	0.30	0.38	0.48	0.66	0.98	1.36
Temperature (°C)	172	173	174	175	176	177	178	179
Weight loss (%)	1.94	2.82	3.88	5.16	6.42	7.60	8.68	9.64

TABLE 7

The 11 selected $g(x)$ functions

No.	$g(x)$	n
1	$\ln[x/(1-x)]$	
2	$x^{1/n}$	0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5
3	$x+(1-x)\ln(1-x)$	
4	$1-\frac{2}{3}x-(1-x)^{2/3}$	
5	$[1-(1-x)^{1/3}]^n$	0.5, 1, 1.5, 2
6	$1-(1-x)^{1/n}$	0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4
7	$[-\ln(1-x)]^{1/n}$	0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4
8	$1/(1-x)^n$	0.5, 1, 1.5, 2
9	$x/(1-x)$	
10	$\ln x$	
11	$[1-(1-x)^{1-n}]/(1-n)$	0.6, 1.1, 1.6, 2.1, 2.6, 3.1, 3.6, 4.1

most probable mechanistic equation $g(x)$ can be selected using the least-squares method and a computer. This gives

$$g(x)=x^{1/5} \tag{3}$$

and the activation energy and pre-exponential factor are found to be 90.1 kJ mol^{-1} and 8.20 s^{-1}, respectively, which are in agreement with the values obtained from the DSC curves using Kissinger's equation. The correlation coefficient was 0.9921.

From eq. (3), we obtain

$$x^{1/5}=k_0t \tag{4}$$

that is

$$x=k_0^5t^5=k_1t^5 \tag{5}$$

in which $k_1=k_0^5$. The decomposition rate is therefore given by

$$\mathrm{d}x/\mathrm{d}t=5k_0^5t^4=k_2t^4 \tag{6}$$

in which $k_2=5k_0^5$.

It can be seen from the above that the reaction rate $\mathrm{d}x/\mathrm{d}t$ of the thermal decomposition of solid NQ crystals increases in the fourth power with time. This fourth-power relationship is characteristic of the topochemical reaction which is also similar to the thermal decomposition processes of $Ca(N_3)_2$, $Pb(N_3)_2$, etc. Thus, the above result further proves that the solid decomposition of NQ crystals obeys a "nucleus formation and growth" type of the "topochemistry", characterised by a period of "nucleus growth", namely an inductive period, in which the reaction rate is very slow, as illustrated by the initial decomposition stage.

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