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INCOMPLETE DECOMPOSITION OF ALKALI METAL AZIDES

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ABSTRACT

The thermal decomposition of sodium azide has been studied in the temperature range 240–360°C in vacuum and under pressure of an inert gas, argon. The results show that the decomposition is partial below 360°C. From the observations made in the present work, namely: (i) the decomposition is incomplete both under vacuum and inert gas; (ii) mass spectrometric studies do not reveal any decrease in the intensity of the background species, CO_2^+, CO^+, H_2O^+, and (iii) sodium metal remains in the 'free state' as seen by the formation of a metallic mirror at temperatures above 300°C, it has been argued that the partial nature of decomposition is due to the confinement of the decomposition to intermosaic regions within the lattice.

INTRODUCTION

A number of ammonium salts are known which decompose incompletely[1–3]. The thermal decomposition of ammonium halates[2] and ammonium perchlorate[1], in particular, has received wide attention. In a typical case of the incomplete thermal decomposition of ammonium perchlorate it has been found that, at low temperatures (below 250°C), the compound decomposes to the extent of 30% only, leaving behind a white residue identical with the original material. It is generally believed that the reasons for the partial nature of the decomposition of ammonium salts lies in the adsorption of NH_3, one of the products of the decomposition, on the decomposing material[4].

The thermal decomposition of sodium azide has also been reported by a few authors[5–7] to be incomplete. Garner and Marke[5], who were the first to study the thermal decomposition of sodium azide in detail, have reported that, even at temperatures as high as 350°C, the decomposition proceeds to the extent of ~85% only. They have suggested that the incomplete decomposition may be due to the adsorption of impurities (NaOH and Na_2CO_3, formed by reaction of Na with H_2O, CO and CO_2) within the crystal. Later, Secco[6] studied the decomposition of single crystals of sodium azide under vacuum and observed that the decomposition was partial upto 350°C, leaving a white residue. They have interpreted the results on the basis of the decomposition proceeding along intermosaic networks. Jacobs and Kureishy[8], who studied the decomposition both under vaccum and a pressure of inert gas, argon, however, do not make any remarks as to the partial nature of decomposition. In their opinion, the incomplete decomposition observed by earlier workers could be due to the faster rate of evaporation of the initially formed sodium nuclei compared with that of the nucleus formation. As a result, the reaction cannot be acceleratory and will soon come to a stop. The results of Walker et al.[7] from their scanning electron microscope studies do not support the above argument. Walker et al. pointed out that the abundance of sodium at the boundary between the decomposed and the undecomposed parts within the crystal (as evident from the photographs of the decomposed material) does not suggest that a premature evaporation of sodium nuclei is responsible for the incomplete decomposition of sodium azide. They suggest that the adsorption of NaOH at reactive sites within the crystal is the reason for the incomplete decomposition of sodium azide. More recently, Torkar et al.[9] have carried out extensive studies on the thermal decomposition of sodium azide. But, they do not report as to whether the decomposition is partial or not.

From the above discussion, it is evident, that there are conflicting views in the literature with regard to the extent of decomposition of sodium azide and the reasons for the partial nature of its decomposition. It has to be mentioned, here, that in the case of ammonium perchlorate, it has been observed, that the extent of decomposition is dependent upon the density of gross-imperfections within the lattice[10]. Moreover, our studies on the effect of dopants and prior mechanical and thermal treatment on the thermal decomposition of sodium azide clearly indicate that the decomposittion nature is sensitive to the concentration of gross defects in the crystal. It is likely, therefore, that the incomplete decomposition of sodium azide, as well as ammonium perchlorate, may not be due to the adsorption of impurities product gases within the crystal but is a consequence of the restriction of the decomposition to "imperfect regions" within the crystal.

Only a few studies[5,11–13] have been carried out on the thermal decomposition of potassium and cesium azides. These azides have not been reported to decompose incompletely.

The present investigation was, therefore, undertaken with a view to:

(a) study the extent of decomposition of sodium azide, at different temperatures, in vacuum;

(b) investigate the effect of the presence of an inert gas, argon, on the decomposition nature of sodium azide;

(c) to find out whether the partial nature of decomposition is characteristic of sodium azide alone or is observed in the case of potassium and cesium azides also; and

(d) seek possible reasons for the incomplete nature of the decomposition of these azides.

EXPERIMENTAL

Sodium azide used in the present work was supplied by Riedel-De Haen AG Selze Hannover. All the samples were reprecipitated twice from double-distilled water by acetone.

Potassium and cesium azides were prepared from the corresponding carbonates (BHD, Analar grade) by reaction with hydrazoic acid. The latter was prepared by the ion-exchange method from sodium azide using Amberlite resin IRC-50(H) (Analar grade, BHD). Both azides were reprecipitated twice from double-distilled water by acetone.

The kinetic studies of the thermal decomposition were followed in a constant volume vacuum line with an initial pressure of 1×10^{-5} Torr. The pressure rise was measured using a McLeod gauge.

All the kinetic runs were carried out on samples having the particle size range of 149 μ–177 μm.

The gaseous products of the decomposition were analysed in an AEI-MS-10 mass spectrometer.

RESULTS

The isothermal decomposition of sodium azide has been studied in the temperature range 240–365°C. Typical plots of the fractional decomposition, α, versus the time, t, of heating are shown in Fig. 1. The decomposition has been found to be incomplete at temperatures below 360°C. By chemical and IR analyses the residue was shown to be identical with the original material. The temperature range 240–365°C could be divided, on the basis of the extent of decomposition, into the fol-

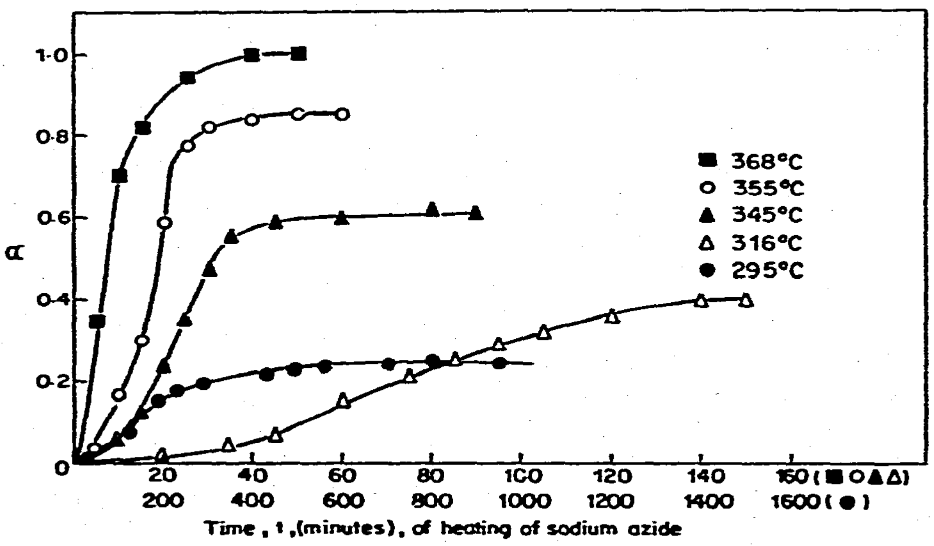

Fig. 1. Plots of the fractional decomposition, α, versus the time, t (m in) of heating of sodium azide.

lowing regions: (A) 240–300°C; (B) 300–320°C; (C) 320–350°C; and (D) 350–360°C, the extent of decomposition, α, being roughly 0.25, 0.4, 0.6 and 0.85, respectively. At temperatures around 365°C the decomposition was observed to go to completion.

At temperatures above 300°C a metallic mirror of sodium appeared on the cooler parts of the reaction tube after the decomposition has proceeded to a certain extent. The time taken for the mirror to appear decreased with an increase in temperature.

The decomposition kinetics of sodium azide have also been studied under a pressure, ~70 mm, of argon gas in the temperature range 275–360°C. The general form of the α–t curves and the activation energy for decomposition were found to be the same as those for decomposition under vacuum. The following observations were made:

(i) The decomposition of sodium azide is partial below 360°C, the extent of decomposition being roughly the same as under vacuum.

(ii) Sodium metal evaporated from the lattice only at temperatures above 350°C.

The decomposition of potassium azide was studied in the temperature range 250–520°C. Plots of the fractional decomposition, α, versus the time, 't', of heating are shown in Fig. 2.

The decomposition of potassium azide has been found to be partial at all temperatures below 340°C. The extent of decomposition being roughly $\alpha = 0.2$. At temperatures above 340°C the decomposition proceeds to completion. It has to be mentioned here that potassium azide melts around 345°C. A metallic mirror of

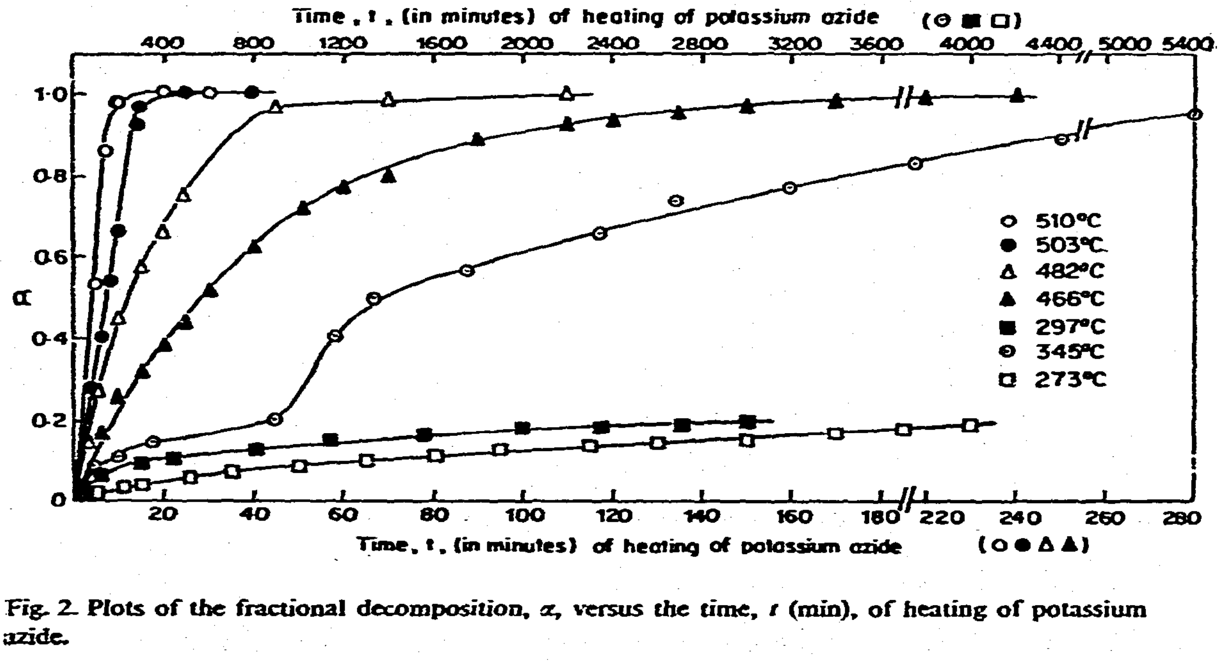

Fig. 2. Plots of the fractional decomposition, α, versus the time, t (min), of heating of potassium azide.

potassium has been observed to appear on the cooler sides of the reaction tube at temperatures above 340°C.

The thermal decomposition of cesium azide has been investigated in the temperature range 250–500°C. Figure 3 represents the plots of fractional decomposition, α, against the time, t, of heating of cesium azide.

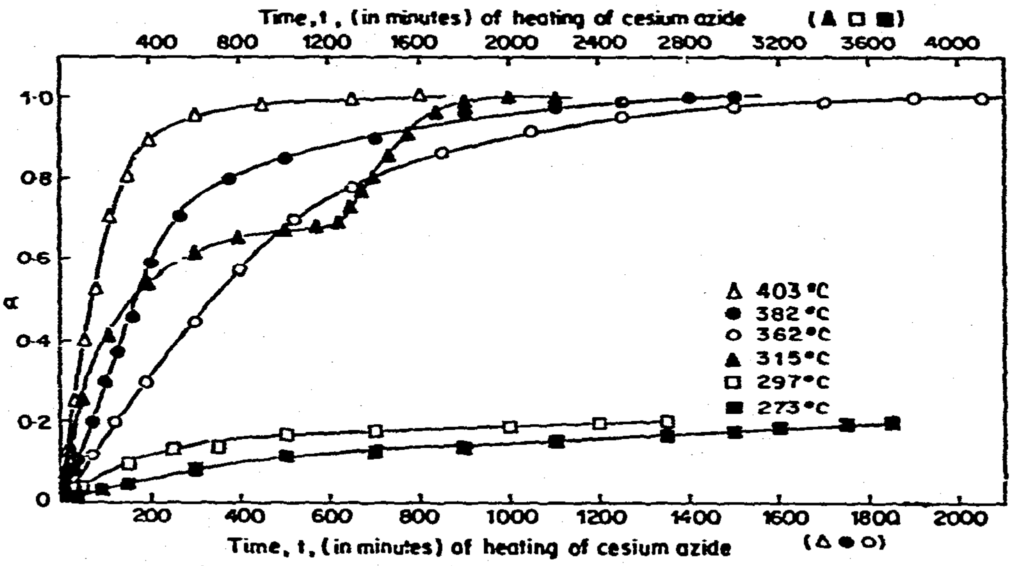

Fig. 3. Plots of the fractional decomposition, α, versus the time, t (min), of heating of cesium azide

The decomposition of cessium azide has also been observed to be partial at temperatures below 320°C, the value of α being 0.2 (The melting point of cesium azide is 315°C). Above 340°C cesium metal evaporated from the lattice.

DISCUSSION

The results of the present study unambiguously establish that the thermal decomposition of sodium azide is partial in nature, below 360°C, both under vacuum and under an ambient pressure of inert gas. The extent of decomposition, however, increases with an increase in the temperature at which the decomposition is carried out. The observations made in the present work on the thermal decomposition of sodium azide under a pressure ~70 mm, of argon gas, namely, that: (i) the extent of decomposition is the same as that under vacuum; and (ii) the decomposition goes to completion only above 360°C, even though the sodium metal remains in the lattice, lead us to the conclusion that the partial nature of decomposition may not be due to the evaporation of sodium nuclei from the sodium azide lattice. A possible reason for the incomplete decomposition could be the adsorption of impurities within the crystal, as suggested initially by Garner and Marke and later by Walker et al. Mass spectrometric results of Walker et al. support this assumption. Results of our

TABLE 1

DECOMPOSITION SPECIES FOR NaN_3 AT 330°C IN A CONSTANT VOLUME SYSTEM CONNECTED VIA A MOLECULAR LEAK TO THE MASS SPECTROMETER

m/e	*Probable assignments*	*Ion current × 10^8*	
		Background species	*Decomposition species*
2	H_2^+	0.01	0.02
4	He^+	0.02	0.02
12	C^+	0.04	0.04
14	N^+	0.08	3.8
15		0.06	0.16
16	O^+	0.06	0.12
17	OH^+	0.50	0.36
18	H_2O^+	1.8	2.2
20	Ne^+	0.01	0.01
22	Ne^+	0.02	0.02
28	N_2^+	2.0	68.0
32	O_2^+	0.2	0.2
36		0.16	0.22
44	CO_2^+	0.18	0.22

mass spectrometric studies (given in Table 1) do not support this suggestion. Nitrogen was found to be the only product of decomposition. In contrast to the observations of Walker et al. the intensity of the background species, CO_2^+, CO^+ and H_2O^+ remained constant and no rare gases (He, A, and Ne) were found to be evolved during the course of the decomposition. These results imply that sodium metal remains in the "free state" and does not form NaOH or Na_2CO_3 by reaction with H_2O, CO_2, CO etc. Moreover, we have observed that a metallic mirror of sodium is formed on the cooler sides of the reaction tube, at higher temperatures (>300°C in vacuum and >350°C under ~70 mm argon gas), during the thermal decomposition of sodium azide. A metallic mirror could not have been observed if sodium had reacted with H_2O, CO_2/CO to form the hydroxide/carbonate.

A plausible reason is that the decomposition is restricted, as suggested by Secco, to the intermosaic network within the crystal. It could be assumed, therefore, that the decomposition of sodium azide comes to a cessation as soon as the "imperfect zones" within the crystal are consumed. Evidence for the present suggestion comes from the facts that

(i) The decomposition extent is temperature dependent. It is quite probable that the concentration of imperfections within the lattice increases with an increase in temperature.

(ii) During the course of our investigations on the effects of dopants and pretreatment, mechanical and thermal, we have found that the decomposition extent is dependent upon the gross-imperfections present in the lattice. Barium ions, and sulphate ions, doped sodium azide, as well as precompressed (at 200 and 300 kg/cm^{-2}) samples exhibit an increases in the extent of decomposition from $\alpha = 0.25$, in the case of pure sodium azide, to $\alpha = 0.35$ in the temperature region 240–300 °C. Moreover, the rate of decomposition was also found to be higher for these samples. However, preheated sodium azide showed a desensitization in the decomposition rate as also a reduction in the decomposition extent from $\alpha = 0.25$ (for untreated Na N_3) to $\alpha = 0.2$. A qualitative inference as to the concentration of gross imperfections in the pure, doped and pretreated samples could be made from the variation in the band widths, at half-adsorption maxima, of the IR absorption peaks, and the broadening of the X-ray diffraction peaks of the precompressed material; and

(iii) the ion currents of the background species, CO_2^+, CO^+ and H_2O^+, do not decrease during the decomposition of sodium azide, thereby suggesting that the sodium metal remains in the free state. (This conclusion is supported by the fact that a metallic mirror of sodium appears at temperatures above 390 °C in vacuum.)

Our results on the thermal decomposition of potassium and cesium azides indicate that these compounds also decompose in an incomplete manner. However, these azides were found to decompose completely at temperatures above their respective melting points. It is unlikely that the reason for their incomplete decomposition is due to, as has been argued earlier[5,7], the adsorption of their corresponding hydroxide/carbonate within the azide lattice. As suggested in the case of sodium azide, the partial decomposition may be due to the fact that the decomposition is confined to the "imperfect regions" within the lattice.

The present work clearly establishes that the alkali metal azides decompose in an incomplete fashion at lower temperatures. It is likely that the reasons for the partial nature of decomposition in azides as well as the ammonium salts are the same. The confinement of the low-temperature decomposition, in these materials, to the intermosaic network within the crystal results in an incomplete decomposition.

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