Thermal analysis of sodium azide

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Abstract

The thermal reaction and decomposition of sodium azide were affected by the gas species, its pressure, sample type (powdered or tablet), particle size, sample weight, surface heterogeneity, additives, aging, etc. In actual experiments, very complicated problems arose because those effects were combined together. In addition, it was determined that heat and mass transfer effects must also be considered when evaluating the thermal reactivity of sodium azide and its mixture.

In this report, the thermal decomposition of sodium azide was mainly studied by thermal analysis, and the factors which affect its thermal properties were discussed.

1. Introduction

As a gas-generating chemical for some safety systems such as air bags, sodium azide is considered as the best material. Many compounds, which contain sodium azide as the main constituent, have been reported as gas-generating agents by many researchers. However, the thermal properties of sodium azide are not very well known as compared with its practical uses.

With regard to the thermal decomposition of sodium azide, kinetic data and an accelerating effect of sodium vapor on the thermal decomposition were reported by Garner et al. [1]. King et al. [2] reported the effect of irradiation using mercury lamp on the thermal decomposition. Sears et al. [3] also obtained results for thermal analysis and determined the effect of atmospheric gas on its thermal decomposition.

In this report, the thermal decomposition of sodium azide was mainly studied using thermal analysis, and the factors which affect its thermal properties were considered.

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2. Experimental

2.1. Materials

Two kinds of sodium azide were used in this experiment. One was supplied by a commercial supplier (designated as "received sodium azide") and had a purity of over 99 wt% and an average particle diameter of 9.2 μm. The other is prepared from an aqueous solution of the received sodium azide by the addition of acetone to this solution ("precipitated sodium azide").

Mechanical treatment was performed using a laboratory vibro-mill (Tutui Scientific Instrumentation Co. Ltd.) using an alumina–ceramic container and 10 alumina–ceramic grinding balls. The vibrational frequency was 100 rpm and the grinding time ranged up to 48 h.

Other reagents obtained from commercial suppliers were prepared by sieving through 325 mesh after drying and purverizing.

2.2. Analysis

Purity was determined from the quantitative analysis using iodimetry. Particle size was determined using Horiba Centrifugal Particle Size Analyzer CAPA-500.

Thermal analysis was performed both with a RIGAKU DTA-TG simultaneous analyzer and high-pressure DTA. Operations were carried out in an alumina open crucible (5 mm i.d. × 5 mm height) at a heating rate 20 °C/min under normal or pressurized conditions using argon, air, helium, nitrogen and oxygen. The sample consisted of 2.0–2.5 mg of nondiluted sodium azide or its mixtures, and was packed in an alumina open crucible in the form of a powder ("powdered sodium azide") or tablet ("sodium azide tablet").

SEM analyses were performed using Nippon Densi scanning electron microscope JCXA 733. Crystallinity was examined using an ordinary X-ray powder diffractometer.

2.3. Aging in various atmospheres

Sodium azide spread as a thin layer on shale was kept in a dessicator at room temperature under flowing nitrogen, oxygen, air, dried carbon dioxide and water-vapour-saturated carbon dioxide. After a specific time period, the sample was taken out and submitted for thermal analysis, X-ray powder diffraction and quantitative analysis of purity in order to evaluate aging effect.

3. Results and discussion

3.1. Thermal analysis of sodium azide

Fig. 1 shows the results of the thermal analysis both of the powdered sodium azide and sodium azide tablet in air. DTA curves of the powdered sodium azide in
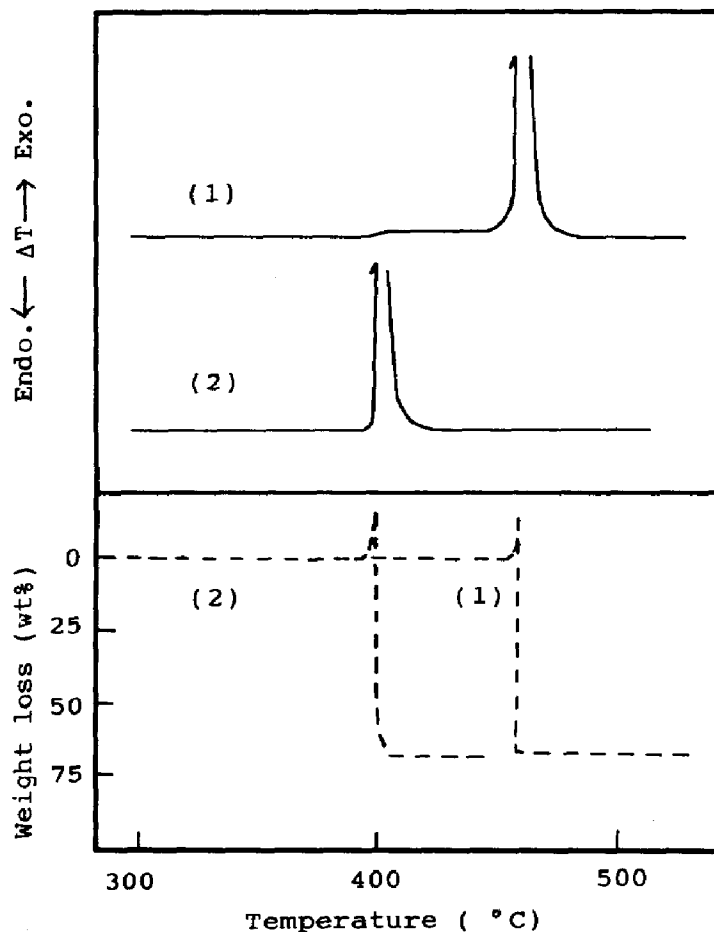
Fig. 1. DTA and TG curves of sodium azide in powder and tablet forms in air: (1) powder; (2) tablet.

air show a small exothermic reaction at 400 °C followed by a large exothermic peak which started at 450 °C and attained a maximum at 460 °C. The temperature of initial small exothermic reaction has a good reproducibility, but that of the latter was very different with each run. The range of scatter for the DTA peak temperature is $\pm$ 9 °C, and the peak temperature of 460 °C is the average value of ten runs.

The small exothermic reaction at 400 °C is ascribed to an oxidation of the surface sodium azide by atmospheric oxygen described by Eq. (1), because this small exothermic reaction could not be detected in inactive gases such as argon that will be described later. On the other hand, reproducibility for the large exothermic reaction at 450 °C will be affected by surface properties such as particle size or surface disorder which will be discussed in Section 3.2.

The latter large exothermic reaction occurred so rapidly that a scattering of sample occurred in the container, but the weight loss was about 60% which corresponded to Eq. (1):

$$2NaN_3 + \tfrac{1}{2}O_2 \rightarrow Na_2O + 3N_2. \tag{1}$$
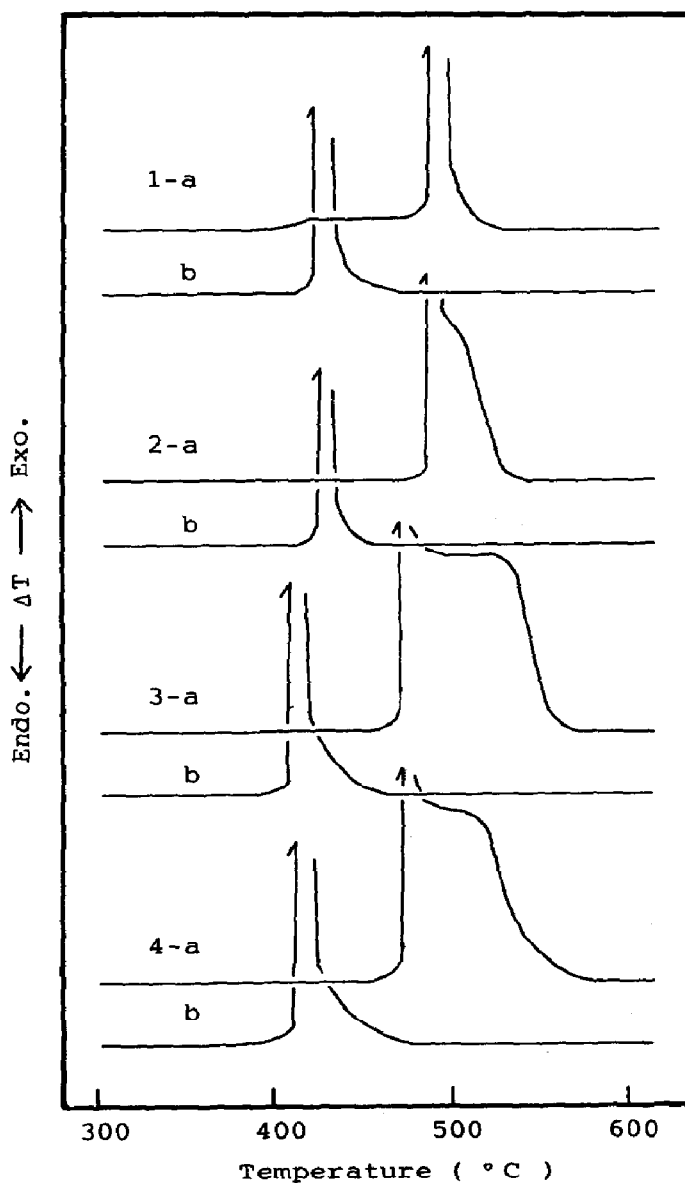
Fig. 2. DTA curves of sodium azide in various gases under normal and elevated pressures: (1) in air; (2) helium; (3) argon; (4) nitrogen; (a) under normal pressure; (b) 50 kgf/cm².

If a sodium azide tablet was submitted for thermal analysis, a larger, more intense exothermic reaction occurred at 402 °C, which corresponded well to the above small exothermic reaction in air. This is important to be considered because heat released by the small exothermic reaction has significantly accumulated compared to the powdered sample and caused the rapid reaction as a result of a heat effect on the reaction using a tablet. With regard to DTA peak temperature, very good reproducibility (± 2 °C) was obtained using a tablet for each DTA run.

In nitrogen, an exothermic reaction occurred at 440 °C accompanying a weight loss of about 5% which corresponded to Eq. (2):

$$NaN_3 \rightarrow Na + \tfrac{3}{2}N_2. \tag{2}$$

This decomposition temperature resembles that in argon (437 °C). A similar reaction also occurred in helium, but the reaction temperature is 460 °C which is slightly higher than that in nitrogen. As stated before, these temperatures not having a very good reproducibility resemble the powdered sodium azide reaction in air ((1) in Fig. 1), and the peak temperatures are average values of ten runs.

If we compare the reaction temperature for the inert gas species, argon has the lowest value, followed by nitrogen and helium. This result is ascribed to the heat transfer effect of atmospheric gas because a gas which has a large thermal conductivity can transfer much of the evolved heat.

3.2. Some factors affecting the thermal analysis of sodium azide

The effect of gas species and its pressure on the thermal decomposition of sodium azide was examined by thermal analysis and the results are shown in Fig. 2. As previously stated, DTA curves of powdered sodium azide at normal pressure in air show a small exothermic reaction at 400 °C followed by a large exothermic peak which started at 450 °C and attained a maximum value at 460 °C. The results for other gases under normal pressure showed no stepwise reaction but showed a large exothermic peak which was different for each specific gas. That is, helium has the highest reaction temperature among the inert gases with a maximum rate at 460 °C. The reason why the reaction rate was different for gas species under normal pressure was ascribed to the heat transfer effect of atmospheric gases. Helium had the largest thermal conductivity among all the gases.

Under elevated pressure, the thermal decomposition of sodium azide is accelerated. The reason why the reaction was accelerated at elevated pressure was ascribed to the repression of mass transfer. That is, accumulation of reaction products on its surface can be accelerated, because the reaction product, sodium, can catalyze the thermal decomposition [1]. Even under elevated pressure, the decomposition rate was different for gas species; this was similar to the normal pressure response. This was also ascribed to the heat transfer effect of atmospheric gases.

Surface characteristics have a remarkable effect on the solid state reaction, especially during its early stage. When sodium azide was milled, its particle size became 4.8 μm after 6 h and 2.5 μm after 48 h. Fig. 3 shows the effect of milling on the thermal reactivity of sodium azide. DTA peak temperature, where the maximum reaction rate is attained, became lower with time. Generally, mechanical milling increases surface heterogeneity such as the amorphous phase on the surface and decreases crystallinity in the neighborhood of the surface. So, milled sodium azide has many active sites on its surface to initiate the reaction. Furthermore, good thermal analysis reproducibility was obtained after milling for 48 h. This is because milling
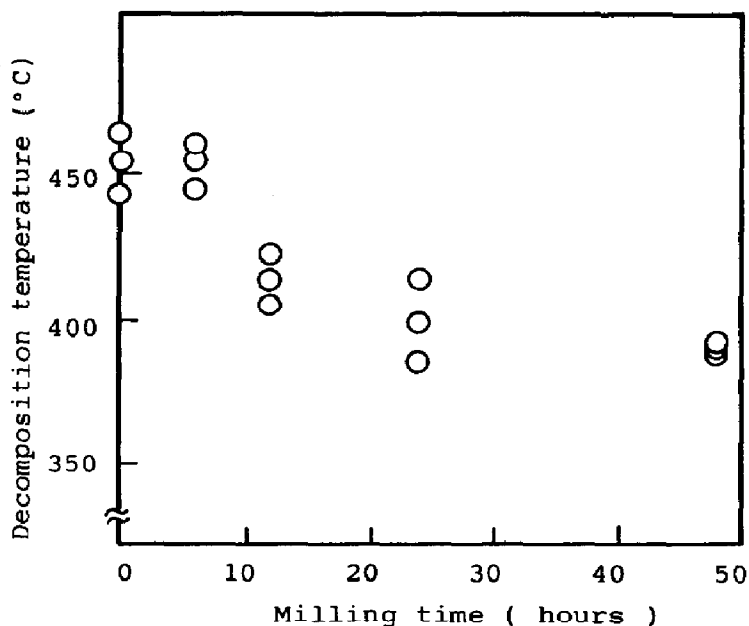
Fig. 3. Effect of milling on the thermal decomposition of sodium azide in argon.

activates the surface to form many germ nuclei for decomposition, which can easily initiates the reaction.

As previously stated, milling increased surface heterogeneity and surface area, both of which affect thermal reactivity. In order to consider only the effect of particle size (the effect of particle size without surface heterogeneity) on the thermal reaction, the thermal analyses were carried out using precipitated sodium azide which was classified through several screens. This classified sodium azide is considered as one without surface heterogeneity. From the results of Fig. 4, the smaller the particle size, the higher the DTA peak temperature. Every class of particles had a clean surface, the reason being ascribed only to a heat transfer effect and not to surface properties. This is considered to be due to the heat flux released from a small particle being high compared to that released from the large particle because of its large specific surface area. So, heat produced by the exothermic reaction of large particles accumulated much more when compared with small particles and the reaction was accelerated by this thermal effect. Fig. 5 also shows the thermal effect, which was confirmed by the thermal analyses carried out using the precipitated sodium azide which was formed into different sample sizes.

Particle size has generally been considered as an index of the surface activity, because performance characteristics of a pyrotechnic composition are affected by the surface area, and the oxidizer and reducing agents contact each other at their surfaces. However, in addition, surface activity is affected by crystallinity, disorder, oxygen deficiency, contamination, adsorbed gases, etc., which are all described as surface heterogeneity properties in this report. As previously stated, vibro-milling also caused an increase in surface heterogeneity accumulating mechanchemical energy on the surface layer.
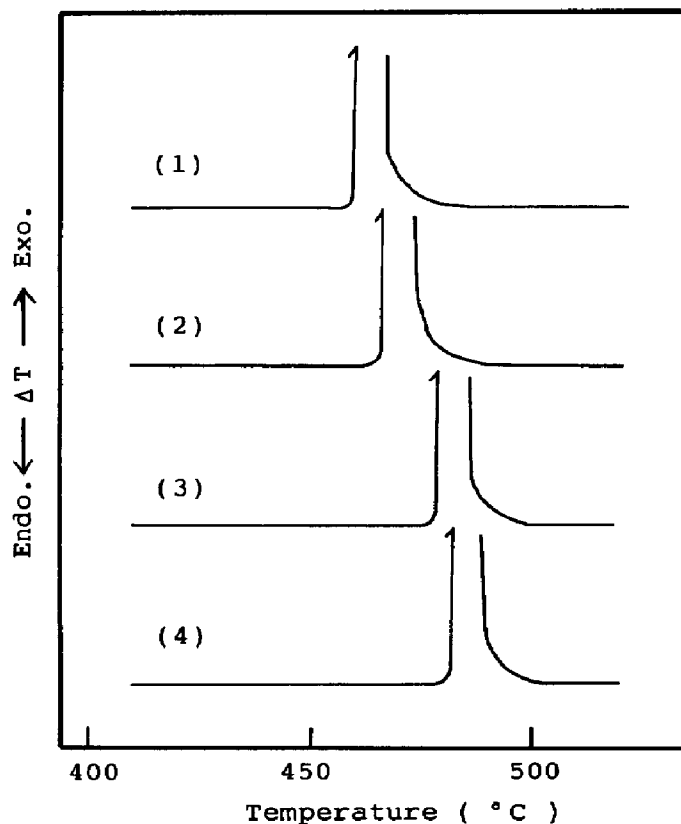
Fig. 4. Effect of particle size on the thermal decomposition of sodium azide in air: (1) over 105 μm; (2) 74–105 μm; (3) 44–77 μm; (4) under 44 μm.
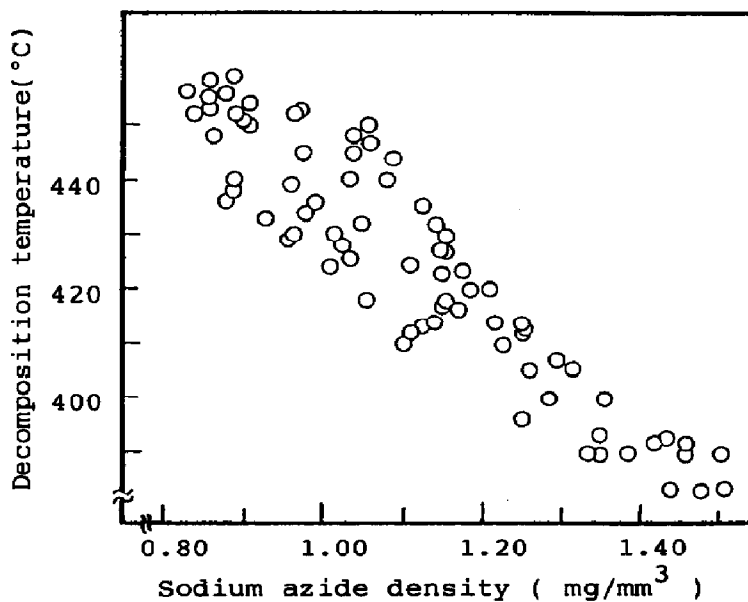

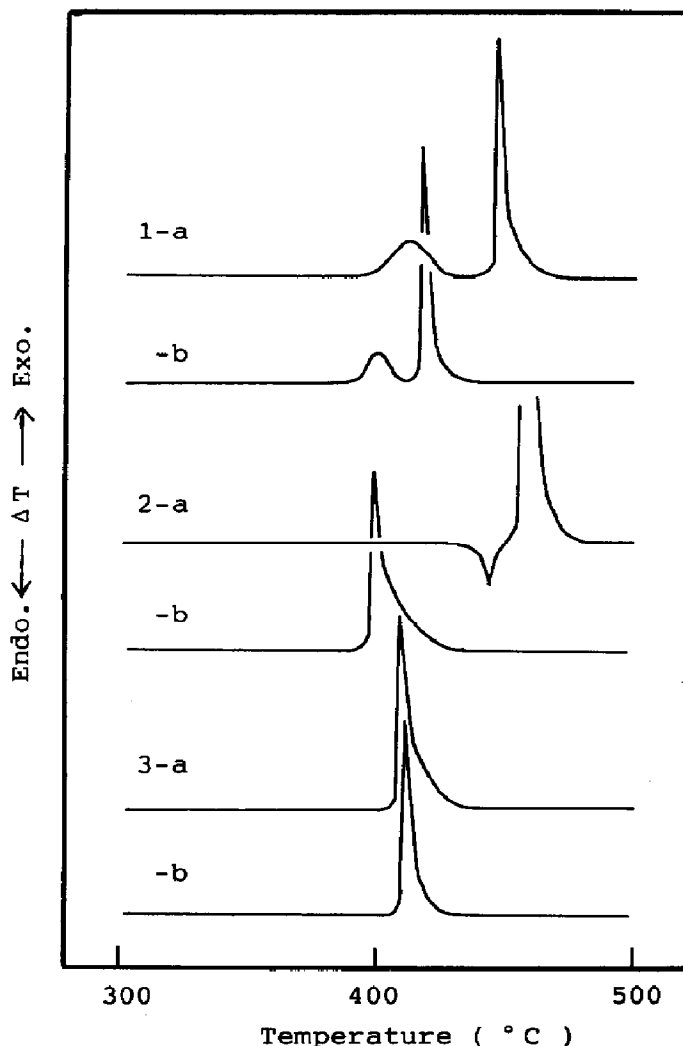Fig. 5. Effect of sodium azide density on its thermal decomposition in argon.

Fig. 6. DTA curves of the mixture of sodium azide with some oxidizers in argon. Oxidizer: (1) manganese dioxide; (2) potassium perchlorate; (3) cupric oxide. Pressure: (a) under normal pressure; (b) 50 kgf/cm².

Many compounds have been examined as oxidizers or additives for sodium azide as gas-generating agents [4]. The results of their thermal analyses are shown in Fig. 6, in which the effect of three representative oxidizers on the thermal reaction of powdered sodium azide were examined in argon. The mixture with manganese dioxide shows two exothermic peaks which resemble those in air shown in Fig. 1. The first peak is a small one ranging from 400 °C to 420 °C followed by a second large, sharp peak at 446 °C. This first small peak was ascribed to the oxidation of sodium azide by active oxygen existing on the surface of the manganese dioxide. Weight loss at the end of the second exothermic reaction amounted to 44 wt% and corresponded well to Eq. (3):

$$2NaN_3 + MnO_2 \rightarrow Na_2O + MnO + 3N_2 \tag{3}$$

The mixture with potassium perchlorate showed a sharp peak at 452 °C immediately after a small endothermic reaction at 440 °C. Optical microscope observations show that this exothermic reaction was caused by the comelting of sodium azide and potassium perchlorate. The mixture with cupric oxide showed a sharp peak at 408 °C. Weight losses for potassium perchlorate and cupric oxide were 55 and 46 wt%, respectively, and corresponded well to Eqs. (4) and (5):

$$8NaN_3 + KClO_4 \rightarrow 4Na_2O + KCl + 12N_2 \tag{4}$$

$$2NaN_3 + CuO \rightarrow Na_2O + Cu + 3N_2 \tag{5}$$
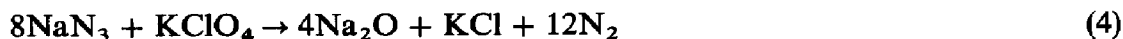
At elevated pressure, the large exothermic reaction was accelerated and the DTA peak temperature became lower for each oxidizer (Fig. 6). However, a small exothermic reaction for manganese dioxide remained unchanged and a small endotherm for potassium perchlorate disappeared.
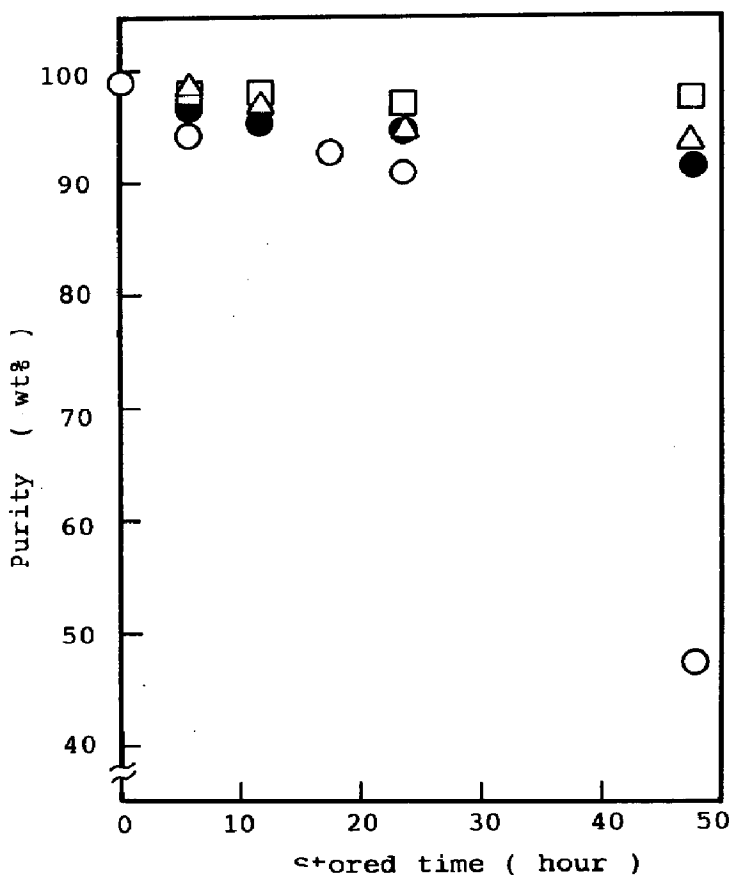

Fig. 7. Aging of sodium azide stored in various atmospheres: (O) in CO_2 saturated by H_2O; (●) dried CO_2; (△) O_2; (□) N_2.

3.3. Aging of sodium azide

Figs. 7 and 8 show the effect of aging on sodium azide's purity and thermal properties, respectively. These results were obtained from the experiments in which sodium azide was exposed in a dessicator at room temperature to flowing nitrogen, oxygen, air, dried carbon dioxide and water-vapor-saturated carbon dioxide. Aging in nitrogen could not be observed after storage for 48 h, and the use of oxygen or dried carbon dioxide also showed only small changes in its purity and thermal properties. On the other hand, sodium azide stored in carbon dioxide saturated with water vapor decreased in purity to 48 wt% of the initial value and lowered its decomposition temperature to 447 °C. In order to examine the reason for this aging, exposed sodium azide after 48 h was analyzed by X-ray powder diffraction and sodium bicarbonate was confirmed to exist (Fig. 9). Furthermore, from the thermal analysis, sodium azide suffering from aging showed a small endotherm at 151 °C caused by the thermal decomposition of sodium bicarbonate and reduced main reaction at 447 °C (Fig. 10).
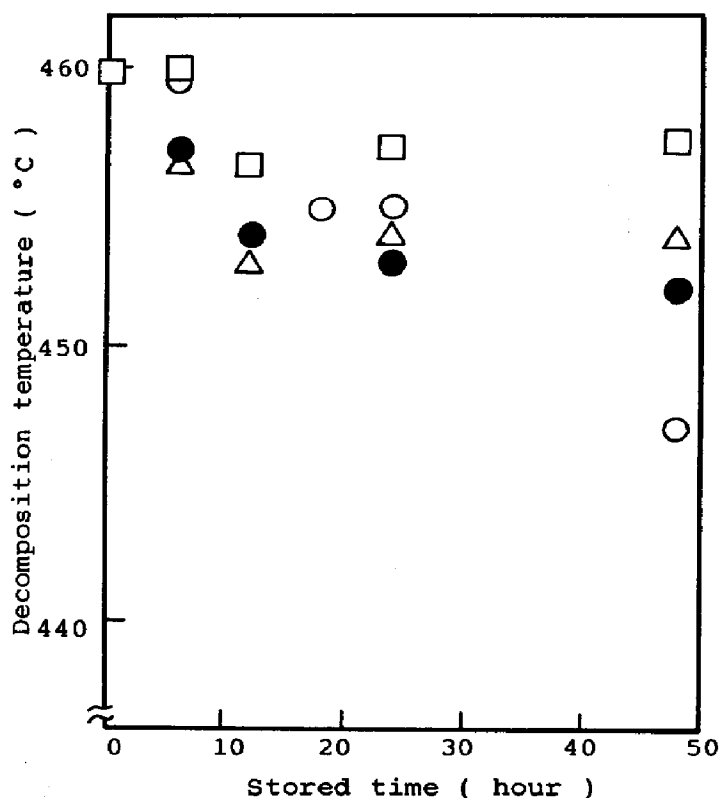

Fig. 8. Effect of aging on the thermal decomposition of sodium azide in argon: (O) in CO_2 saturated by H_2O; (●) dried CO_2; (△) O_2; (□) N_2.

Fig. 10. Thermal analysis of sodium azide after aging and sodium bicarbonate in argon: (1) sodium azide after aging; (2) sodium bicarbonate.
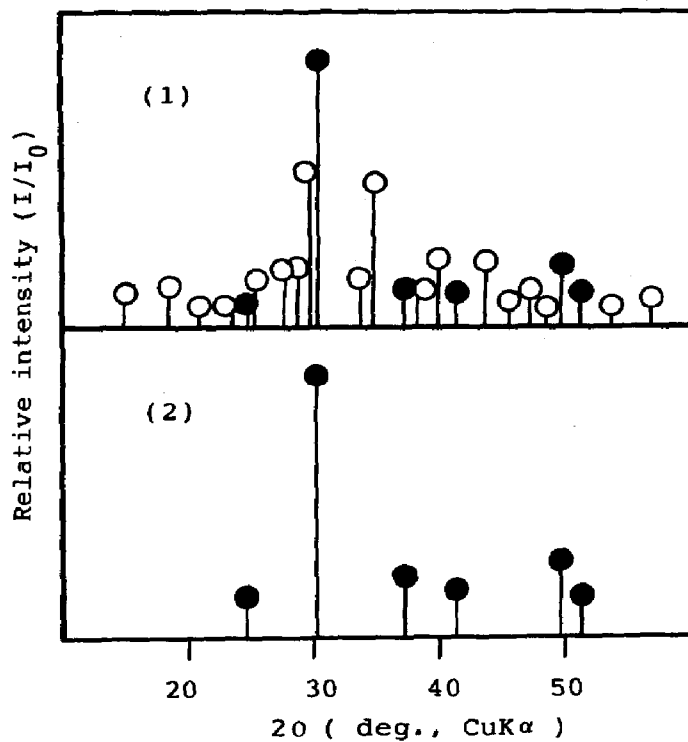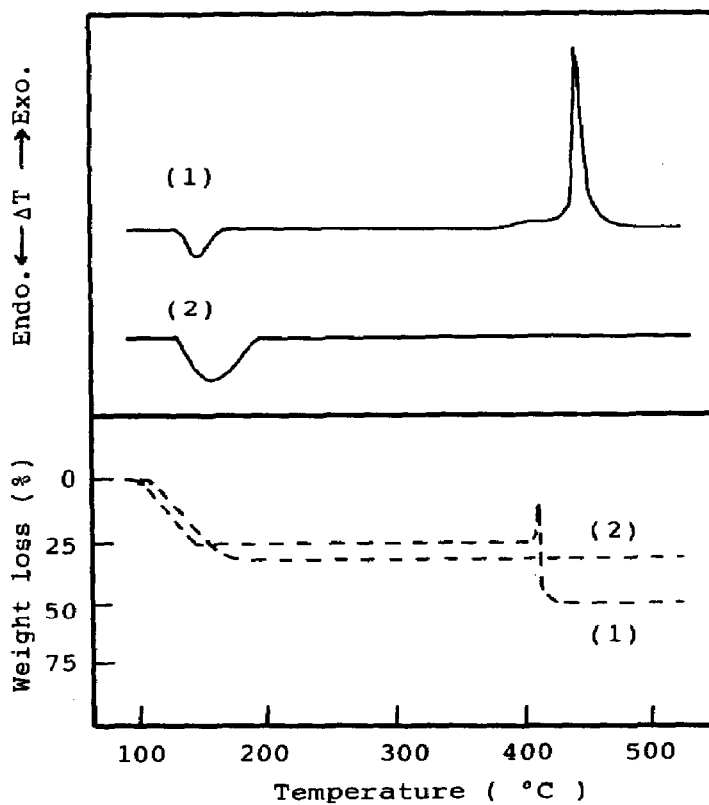
Fig. 9. X-ray diffraction patterns of sodium azide after aging: (1) sodium azide after aging; (2) sodium bicarbonate; (○) sodium azide; (●) sodium bicarbonate.

4. Conclusions

The thermal reaction and decomposition of sodium azide were affected by gas species, its pressure, type of sample (powdered or tablet), particle size, surface heterogeneity, additives and aging, etc. Very complicated problems arose in actual experiments because these effects were additive. In addition, it was found that heat and mass transfer effects must also be considered when evaluating the thermal reactivity of sodium azide and its mixture.

References

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