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Thermal decomposition of γ-irradiated zinc hydroxy azide

S R YOGANARASIMHAN and C R JAGGA*
Explosives Research and Development Laboratory, Defence Research and Development Organisation, Ministry of Defence, Pashan, Pune 411 021, India.
* ITMME Centre, Department of Mechanical Engineering, Indian Institute of Technology, New Delhi 110 029, India.

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Abstract. The effect of pre-irradiation by γ-rays (^{60}Co) at varying dosages on subsequent thermal decomposition of differently treated samples of zinc hydroxy azide is reported here. The same kinetic forms as in the case of untreated sample, viz., the unimolecular decay law followed by the contracting cube, fit the a,t data. The rate constants increase only marginally. The effect of increasing dosage from 10 krad to 24 Mrad is very small. The effect of pre-irradiation on decomposition of the aged sample is slightly more pronounced than in the case of the fresh sample.

Keywords. Gamma-irradiated zinc hydroxy azide; thermal decomposition; kinetics of decomposition.

1. Introduction

The mode of decomposition of solids, particularly azides and other explosive materials, is sensitive to disturbing influences such as artificially incorporated defects, pre-irradiation and pre-heating. Thomas and Tompkins (1951) reported an increase in the acceleratory rate and decrease in the power law exponent from 6 to 3 in the thermal decomposition of UV-irradiated BaN_6. A similar but more pronounced effect has been observed by Prout and Moore (1966) for the same compound irradiated with γ-rays. In the case of ammonium perchlorate (Herley and Levy 1973), pre-irradiation with γ-rays shortened the induction period and markedly increased the rate of decomposition during the acceleratory period. Some substances, however, do not show any change in decomposition kinetics when irradiated prior to heating. Pre-irradiation of barium styphnate (Tompkins and Young 1956), for example, with UV light does not affect the decomposition, and lead styphnate (Flanagan 1962) is reported to be the most radiation-resistant among the explosives. Yoganarasimhan and Jagga 1980 a recently reported the kinetics of thermal decomposition of unirradiated zinc hydroxy azide. In an attempt to understand the radiation damage of zinc hydroxy azide, the effect of pre-irradiation with γ-rays on subsequent thermal decomposition of the compound is being reported here.

2. Experimental

Out of the two differently prepared samples of the compound investigated earlier (Yoganarasimhan and Jagga 1980 a), the one with composition $Zn(OH)_{2-x}(N_3)_x$ ($x = 1{\cdot}09$) was employed for the present study, since this sample was considered to be much closer to the stoichiometric zinc hydroxy azide. A part of the sample was kept apart under dry conditions in vacuum for ageing for about 8–10 months. On prolonged ageing the azide content of the sample increased and corresponded to the composition $Zn(OH)_{2-x}(N_3)_x$ ($x = 1{\cdot}16$), probably as a result of dehydration.

Pre-irradiation with γ-rays ($\sim$ 1 MeV) from ^{60}Co source was carried out on the fresh and the aged samples contained in sealed evacuated pyrex glass ampules. A constant weight of the sample (10 mg) was irradiated with a given dose, the dosages varying between 10 krad and 24 mrad. The conventional method of analysis of azides [Van der Meulen (1948)] did not reveal any appreciable difference in the nitrogen contents of the unirradiated and irradiated samples. There was no measurable decay of the effect of irradiation on storage of the irradiated samples under dry conditions.

Thermal decomposition kinetics were studied in a conventional high vacuum system. The pressure of nitrogen developed in a constant volume system was recorded as a function of time. The degassing correction was applied to the recorded pressures at all temperatures before calculating the fractional decomposition.

3. Results

The results of the kinetic measurements of the decomposition of the fresh and the aged samples irradiated prior to decomposition are summarised below.

3.1. *Fresh sample*

The sample was pre-irradiated with 2·5 mrad, 11·4 mrad and 20 mrad of γ-rays and the decomposition was studied subsequently at different temperatures.

(i) The same kinetic forms as in the case of untreated sample, i.e., the monomolecular decay law followed by the contracting cube, describe the α, t data. The plots of decomposition of the 11·4 mrad sample and the unirradiated sample at different temperatures are shown in figure 1.

(ii) The rate constants increase only marginally and the effect of increasing dosages is observed to be small.

3.2. *Aged sample*

The sample was pre-irradiated with 10 krad, 1 mrad, 2 mrad and 24 mrad of γ-rays and decomposition kinetics of the differently irradiated samples were compared with those of the untreated sample, at different temperatures.

(i) The rates of decomposition of pre-irradiated samples are higher than those of the untreated samples. The effect of 24 mrad of pre-irradiation on decomposition rates at three different temperatures is shown in figure 2.

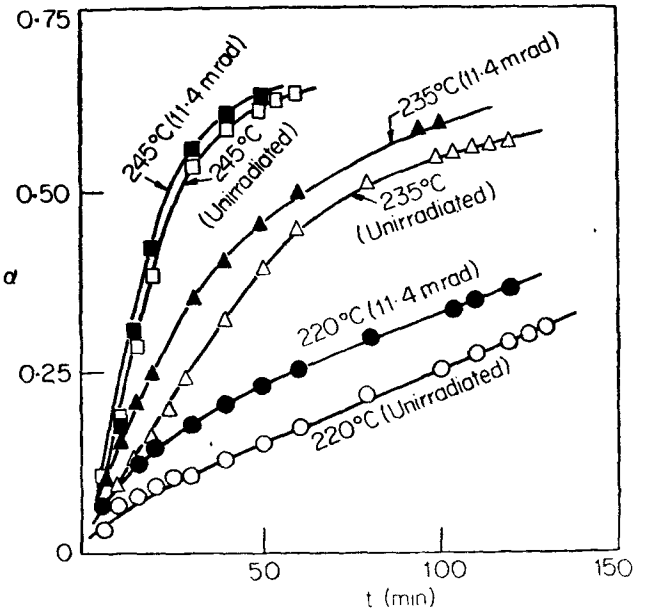

Figure 1. Thermal decomposition at different temperatures of fresh zinc hydroxy azide, pre-irradiated with γ-rays.

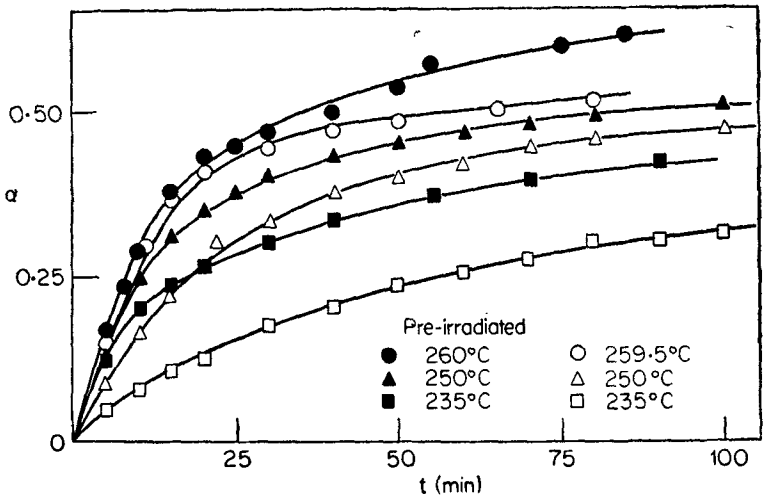

Figure 2. Thermal decomposition at different temperatures of the aged sample of zinc hydroxy azide, pre-irradiated with 24 mrad.

(ii) A slightly favourable effect of increasing dosage of irradiation with respect to the rate of decomposition is evident in figure 3. The effect levels off at higher dosages.

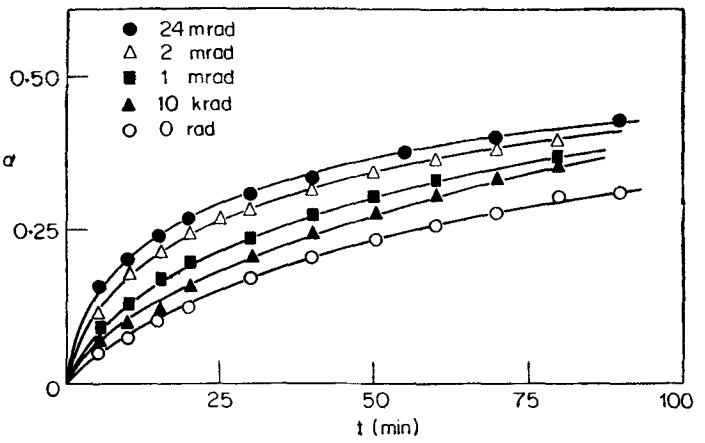

Figure 3. Decomposition at 235° C of the aged sample, pre-irradiated with different dosages.

4. Discussion

The results recorded above show that promotion of rates of thermal decomposition of zinc hydroxy azide by pre-irradiation with γ-rays is only of marginal magnitude. A similar trend has been observed in the case of fresh sample of zinc azide (Yoganarasimhan and Jagga 1980b) which also follows the same deceleratory kinetics as zinc hydroxy azide. A perusal of literature on systems studied so far reveals that the effect of pre-irradiation is much more pronounced generally in the case of sigmoidal decompositions where the number of potential nucleus formation sites increases with time and an induction period precedes the main decomposition reaction. The role of pre-irradiation in such cases is reported (Herley and Levy 1973) to introduce additional decomposition nuclei (dislocations, etc.) by radiolytic decomposition in the solid and therefore reduces the induction period and accelerates the decomposition rate. From the present investigations on pre-irradiated zinc hydroxy azide samples one could possibly infer that the effect of pre-irradiation in enhancing the nucleation process in deceleratory mode of decomposition is not of much significance. The controlling factor for decomposition is the number of nucleus-formation sites and it is very large in these samples as evidenced by their exponential consumption in the initial region of decomposition. To observe any detectable effect of pre-irradiation in increasing the number of decomposition nuclei in these samples, the dose has still to be much greater than the maximum given by us. The observed, though small, enhancement in the rates of thermal decomposition of the pre-irradiated samples of zinc hydroxy azide shows that the compound is not resistant to γ-radiation.

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