

Thermal Decomposition of UV-irradiated Barium Azide

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The thermal decomposition of three differently obtained anhydrous samples of barium azide and the effect of short-period pre-irradiation with UV light on their subsequent thermal decomposition have been studied. The kinetic data are best fitted into the Avrami-Erofeyev equation with $n=4$. The observed rates of decomposition of samples obtained from hydrates are lower than that of the sample obtained anhydrous. The role of deep surface traps and excess cation vacancies which scatter the excitons has been invoked to explain the observed differences in the rates of decomposition. The effect of pre-irradiation in activating the deep surface traps and accelerating the rate of growth of small nuclei has been discussed. The effect of radiation induced defects N_2 and N_4 on decomposition has also been discussed.

THE effect of pre-irradiation on thermal decomposition of barium azide has been extensively studied¹⁻⁵. Garner and Maggs¹ studied the effect of pre-irradiation with UV light and noted a shortening of induction period and increase in the maximum velocity of the reaction with increasing dose of irradiation. Thomas and Tompkins² employed power law for the analysis of kinetic data. They reported a 100-fold increase in the rate of thermal decomposition of $Ba(N_3)_2$ pre-irradiated with UV light. They further noted that pre-irradiation is more effective, beyond a certain critical dose, in shortening the induction period and decreasing the exponent in the power law from 6 to 3. Analysis of the kinetics of thermal decomposition of unirradiated and γ -irradiated $Ba(N_3)_2$ by Prout and Moore³, using the Avrami-Erofeyev equation with $n=4$ showed that the increased dose brought about a drastic reduction in the induction period, increase in the velocity constant and steady fall in the inflexion points of the pressure-time plots.

So far only the anhydrous $Ba(N_3)_2$ obtained from the monohydrate has been the subject of such a study and the effect of pre-irradiation on the decomposition of the sample prepared as anhydrous⁶ is not reported in the literature. It was considered worthwhile to study the thermal decomposition of such a sample pre-irradiated with UV light.

Materials and Methods

$Ba(N_3)_2$, $Ba(N_3)_2 \cdot H_2O$ and $Ba(N_3)_2 \cdot 1\frac{1}{2} H_2O$ were prepared by the method reported by Torkar *et al.*⁶. The samples were completely dehydrated by evacuation over P_2O_5 . [The samples so obtained are referred to in the text as $Ba(N_3)_2$ I, II and III respectively]. The samples were all uniformly aged for about three months and the particle size was between -275 and $+325$ mesh (Tyler standard).

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Chemical and spectrographic analysis showed that the azide samples were better than 99.97% pure. The percentage of some of the major impurities were Fe, 0.0005; Ca, 0.005; Sr, 0.003; Na, 0.004; and Cl, 0.003.

For a typical pre-irradiated thermal decomposition run, the sample (1-1.5 mg) was spread uniformly at the bottom of the pyrex bucket and irradiated, at 0° , with a low-pressure mercury lamp having a strong emission at 2537\AA . For each pre-irradiated run, the sample was irradiated for the required time, evacuated for 30 min to out-gas the accumulated gas and then raised to the decomposition chamber maintained at a constant temperature. The nitrogen pressures during the subsequent thermal decomposition were recorded as a function of time.

The degree of decomposition, α , was calculated from the measured nitrogen pressures, considering that 75% of the azide decomposed to give nitride⁷.

The samples were pre-irradiated to different dosages and their subsequent thermal decomposition was studied at 105° .

Results

Unirradiated barium azide — A knowledge of the decomposition of the unirradiated salt was necessary before studying the effect of UV irradiation. The pressure-time plots were fitted into power law equation with different exponents ranging from 3 to 6, and also Avrami-Erofeyev equation^{8,9},

$$f(\alpha) = [-1n(1-\alpha)]^{1/n} = k(t-t_i) \quad \dots(1)$$

where $n=4$, $\alpha = p/p_f$ and t_i is the length of the induction period, p_f being the final pressure theoretically possible after complete decomposition of the material taken. The decomposition was followed up to about $\alpha = 0.3$ and t_i has been taken to be the time corresponding to $f(\alpha) = 0.1$, during which no measurable amount of gas is evolved. The results show that the rate of decomposition follows the order $Ba(N_3)_2$ I > II > III.

Pre-irradiated salt—The three samples were irradiated at constant intensity for different periods of time (up to 2 min) and then thermally decomposed at the same temperature as the unirradiated samples. The typical pressure-time curves for different dosages in the case of $Ba(N_3)_2$ II are shown in Fig. 1. The kinetic data for all the samples have been plotted using the A-E equation. The effect of pre-irradiation on the rate constant and induction period as a function of dosage in all the three samples is shown in Fig. 2. The significant results are:

- (i) The values of the rate constant, k , increase with increase in dosage and eventually reach a saturation value.
- (ii) The induction period remains practically constant in the case of sample I. With the other two samples, however, there is an initial sharp fall in the induction period which subsequently approaches saturation with increase in dosage.
- (iii) The deviation from the A-E equation, manifest as lowering of the inflexion points follows the order III > II > I for the same time of irradiation.

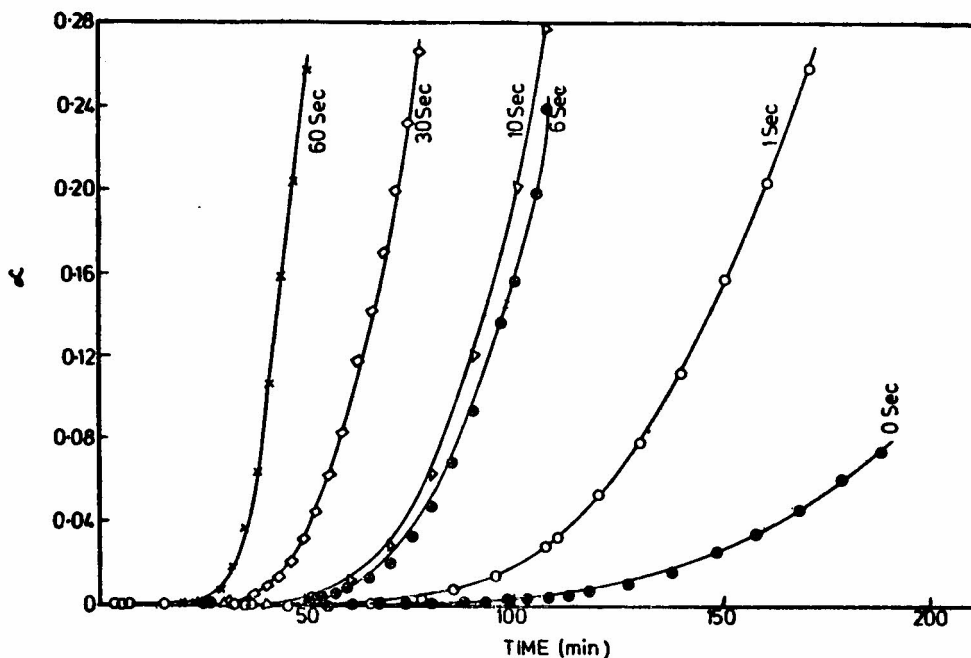


Fig. 1 — α - t plots for thermal decomposition of sample-II pre-irradiated for different periods

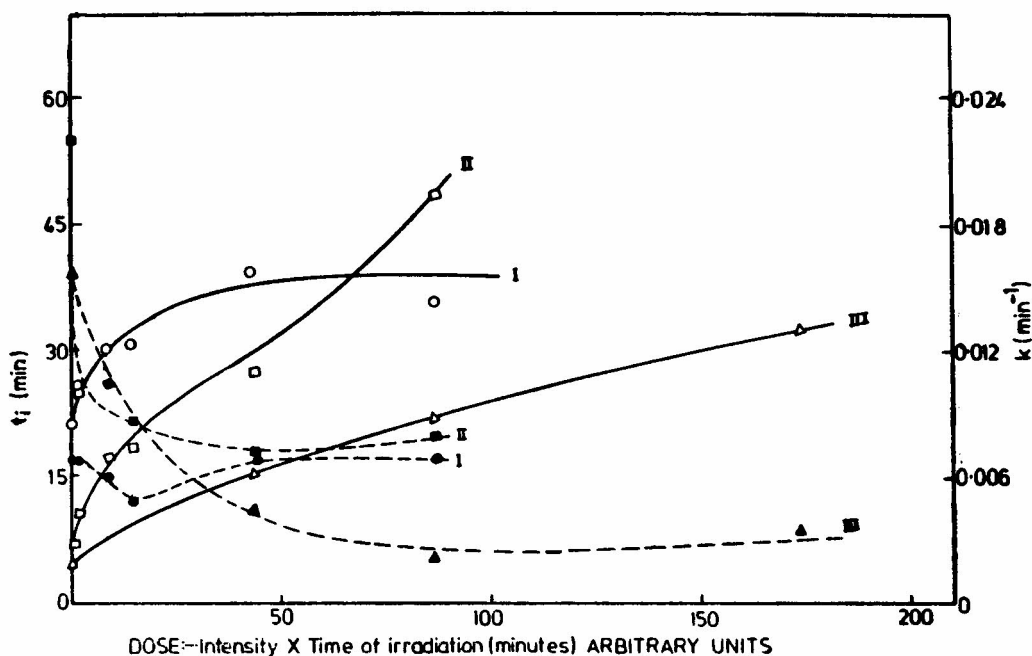
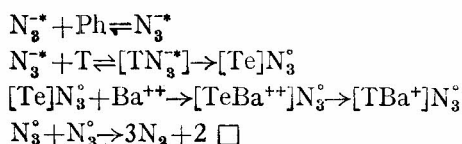


Fig. 2 — Plots of induction period vs dose (broken lines) and k vs dose (continuous lines) for the three samples I, II and III

Discussion

The large band gap, about 8.5 eV, of barium azide¹⁰ forbids conduction electrons to be involved in thermal decomposition. Consistent with their new experimental data, Torkar, Spath and Herzog modified an earlier theory proposed by Tompkins and coworkers² involving the formation of mobile excitons, N₃^{*}, by thermal excitation process. These excitons can either return to the ground state or after collision, be reversibly trapped at some lattice imperfections. The trapped excitons undergo, through thermal energy, electron transfer giving trapped electron — shared among surrounding cation — and holes bound to the complex. These complexes act as germ nuclei. The growth of these small nuclei takes place by electron transfer from the adjacent azide ion to the nucleus, giving a Ba atom (and two anion vacancies) which is stabilized by interaction with adjacent Ba²⁺ ion. The propagation of these electron transfer steps leads to aggregation of small nuclei to the metal speck of critical size which acts as an active growth nucleus.



Ph = phonon, T = trap and \square = anion vacancy
Chart 1

Such a mechanism (Chart 1) along with a growth process involving an electron transfer from an adjacent N₃ ion resulting in a Ba atom and two anion vacancies gives rise to a power law¹⁰, $\alpha = kt^4$. For small values of α as we have in the present case, namely in the acceleratory period, the power law is equivalent to the A. E. equation with $n = 4$.

Young¹¹ has stressed the importance of amorphous regions of the lattice in the process of nucleus formation. A hydrate crystal when exposed to vacuum over P₂O₅ is supposed¹² to give a metastable, partly amorphous, anhydrous phase which undergoes further rearrangement thereby creating cracks, channels and surfaces. Sample III is more susceptible to the process of rupture and rearrangement of lattice because of larger water of hydration. The samples obtained from hydrate, therefore, have greater number of amorphous regions and hence greater number of small nuclei around a growing nucleus. This has the effect of increasing the disorder in the lattice by increasing the strain at the reaction interface, with a consequent increase in the entropy of transition state. The experimentally determined pre-exponential factors for the samples I, II and III are 10¹³, 10¹⁹, 10^{19.5} respectively (unpublished work of Tompkins and Yoganarasimhan). At least a part of increase in this factor in samples II and III must be due to increase in entropy of activation. It is possible that about 10¹³ nuclei are in normal positions distributed fairly uniformly in addition to a large number of nuclei in special positions. Because of incoherence of reaction interface in highly disordered samples II and III, the growth of satellite nuclei takes place

more slowly in areas surrounding these special positions. This manifests as slower rates of decomposition and longer induction periods in samples II and III.

Another factor which is responsible for the slow rate of decomposition of samples II and III is probably the existence of deep surface traps. In addition, several ionic crystals have a negative potential between the surface and the bulk due to the presence of excess cation vacancies at the surface. The cation vacancies by virtue of their negative charge can scatter electrons very strongly thereby preventing the electron transfer from excitons to the Ba²⁺ ion. The result would be a lowering in the rate of nucleation in samples of barium azide which have high internal surfaces.

Effect of pre-irradiation — Interaction of UV radiation with the structural singularities caused by dehydration and the role of radiation induced defects are to be visualized to explain the effect of pre-irradiation on thermal decomposition of the three samples. The ESR absorption study of anhydrous barium azide¹³, UV-irradiated at liquid nitrogen temperature suggests the formation of N₂⁻ and N₄⁻ centres. The absorption of the 2537 Å radiation produces excited azide ions. While the excited azide ions formed in the perfect crystal simply revert to the ground state, those which are formed adjacent to the existing imperfections like impurity ions, vacancies dislocations, etc., where the selection rules are relaxed, can decompose as shown in Chart 2.

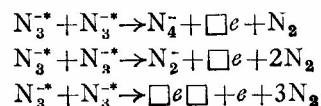
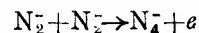


Chart 2

On warming the irradiated Ba(N₃)₂ from low temperature to the room temperature, the N₂⁻ species bleach as:



The N₄⁻ centre is stable at room temperature and has even survived 45 min at 100° without appreciable annealing. Its stability will depend upon crystal structure and the trapping centres. The crystal structure of the three samples of anhydrous barium azide is essentially the same (Yoganarasimhan and Tompkins, unpublished results). However, the higher defect concentration in samples II and III will give rise to greater number of N₄⁻ and F-centres. The rate of N₂⁻ formation increases with increasing dose of irradiation, with subsequent saturation. The influence, if any, of radiation induced defect N₄⁻ on the subsequent thermal decomposition seems to be negligible, unless these species, on bleaching, interact with the existing defects.

The effect of pre-irradiation on thermal decomposition could be explained on the basis of the vast difference in the defect concentrations of the three samples. The structural singularities give rise to discontinuities in the periodic potential of the perfect lattice. The result would be creation of additional levels in the band gap. Thus several additional exciton levels will become available favouring the excitation processes. Secondly, the traps themselves,

namely cation impurities, anion vacancies and surfaces may get activated by interaction with the radiation. The deep traps can now function effectively for bringing about the bimolecular decomposition of the excitons. With the increase in trapping efficiency, the rate of subsequent thermal decomposition obviously increases. The very large increase ($\approx 450\%$ w.r.t. the rate of decomposition of un-irradiated salt) for a 60-second irradiation period in the case of sample III compared to about 100% in the case of sample I should obviously be due to the large concentration of surface traps which can be activated in the former sample. A similar argument holds good for the sample II.

Induction periods—The induction period is attributed to the slow growth of nuclei. It is the time taken for the nucleus to grow to the critical size for normal growth. If the rate of slow growth is accelerated by some means, the induction period will be decreased. Pre-irradiation helps the process by converting the embryos, i.e. the small nuclei into enlarged germ nuclei, by photolytic decomposition¹⁴, so that they do not have to grow for such a long time before they reach critical dimension for normal growth in the subsequent thermal decomposition. This effect will be more in samples II and III because of greater population of small nuclei in them. Consequently, t_i falls considerably in these samples

after pre-irradiation with lighter doses. In sample I there is no effect of pre-irradiation on slow growth, probably because of scarce concentration of micro-nuclei.

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