Thermal decomposition of zinc hydroxy azide

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Abstract. The isothermal decomposition of zinc hydroxy azides, $Zn(OH)_{2-x}(N_3)_x$, follows deceleratory kinetics throughout the temperature range studied. The initial part of the decomposition fits into unimolecular decay law, $\log (1 - a) = - kt$. The contracting volume law satisfactorily describes the data at higher degrees of decomposition. The maximum value of a upto which the slow decomposition could be recorded was 0.75. The aged form of zinc hydroxy azide decomposes with much lower rates and slightly different topochemical characteristics. The decrease in the rate of decomposition on ageing has been attributed to the formation of carbonate on the surface of the compound during storage. The change in topochemical behaviour is traced to the reported layer structure of zinc hydroxy azide. The effect of pre-heating on subsequent thermal decomposition has also been discussed.

Keywords. Thermal decomposition ; zinc hydroxy azide ; kinetics of decomposition; ageing effect.

1. Introduction

Early work on zinc hydroxy azide was confined to its preparation (Curtis and Rissom 1898) and structural analysis (Feitknecht and Zschaler 1957). The compound with exact stoichiometry $Zn(OH)N_3$ is extremely difficult to prepare and invariably one ends up with a nonstoichiometric composition $Zn(OH)_{2-x}(N_3)_x$, where x can have widely different values depending upon the method of preparation of the sample. This is not unusual, for there exist several compounds of zinc particularly basic carbonate and basic chloride which do not have stoichiometrically simple composition. Detailed studies on kinetics of thermal decomposition of zinc hydroxy azide have not been reported so far. Even the topokinet characteristics, let alone the mechanism of its thermal decomposition have remained unknown. We are concerned here with a mechanistic study on its isothermal decomposition. Though the limitations of the kinetic approach are fully realised, the difficulties in preparing and carrying out other useful physico-chemical measurements of zinc hydroxy azide with erratic stoichiometry have constrained us to rely predominantly on the kinetic approach itself.

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Many metallic azides can be prepared in a state of high purity and decompose practically stoichiometrically to the metal and nitrogen in convenient temperature ranges. They are therefore particularly suitable for investigating decomposition of the general type

$$A\,(s) \to B\,(s) + C\,(g). \tag{1}$$

Though the decomposition of zinc hydroxy azide belongs to the above type and can be explained in relation to the established topochemical models for the solid state decomposition reactions, the role of the solid product is difficult to analyse in a manner done in pure metal azides (Prout and Moore 1966; Bartlett *et al* 1958). This difficulty springs up especially because of the possibility of dehydration of the basic azide to an uncertain composition $x\mathrm{Zn}\,(\mathrm{N_3})_2 \cdot y\mathrm{ZnO}$ prior to the start of its decomposition to gaseous nitrogen.

The kinetics of isothermal decomposition of two differently prepared samples of zinc hydroxy azide are interpreted in terms of instantaneous nucleation followed by rapid surface growth. It is known that different rate expressions may be obtained with a particular compound due to slight variation in the method of preparation or to different degrees of ageing of the samples of the same preparation. This conclusion has been demonstrated in the decomposition of silver oxalate (Finch *et al* 1954), barium azide (Yoganarasimhan 1968) and zinc azide (Jagga 1977). In view of this, a part of the compound under study was stored in dark under dry conditions for about one year and the effect of ageing on its subsequent thermal decomposition is reported here. The effect of pre-heating on the decomposition of the aged sample has also been studied.

2. Experimental

The composition of zinc hydroxy azide is highly susceptible to methods of its preparation. Sample 1 was obtained by slow evaporation of a dilute aqueous solution of zinc azide. The mass left behind was in the form of flakes and corresponded to the formula $\mathrm{Zn(OH)}_{2-x}(\mathrm{N_3})_x$ ($x = 0 \cdot 86$). The sample was ground to a fine powder ($- 250 + 325$ mesh) and stored under dry conditions for about 8 months before studying its decomposition. The value of x rose to $0 \cdot 92$ at the end of ageing. Sample 2 was prepared by exposing the normal zinc azide $\mathrm{Zn(N_3)_2}$ to moist atmosphere with controlled relative humidity for several days and then ground to the size $- 200 + 250$ mesh (BSS). Its stoichiometry determined after about one month of its preparation corresponded to $\mathrm{Zn(OH)}_{2-x}(\mathrm{N_3})_x$ ($x = 1 \cdot 09$). This sample shall be referred to as the fresh one. Sample 3 is a part of the sample 2 aged for about one year. The nitrogen and zinc content of the sample were determined several times during the storage. The azide content increased from $1 \cdot 09$ to $1 \cdot 16$, probably as a result of dehydration under dry condition of ageing as

$$2\,\mathrm{Zn(OH)}_{2-x}(\mathrm{N_3})_x \rightleftharpoons (2 - x)\,\mathrm{ZnO} \cdot x\mathrm{Zn(N_3)_2} + (2 - x)\mathrm{H_2O}. \tag{2}$$

Zinc was determined by titration against EDTA and the nitrogen content determined by the method described by van der Meulen (1948).

Thermal decomposition was carried out in a conventional high vacuum line consisting of diffusion pump, McLeod gauge, traps, decomposition chamber, etc. 2 to 3 × 10⁻⁶ kg of the sample was accurately weighed in a bucket, introduced into the decomposition chamber and evacuated for 24 hr before studying the decomposition kinetics. The temperature was maintained by an electronically controlled furnace correct to ± 0·25° C. Degassing corrections were applied to the pressures recorded in a system of known constant volume before the degree of decomposition was calculated.

3. Results

The primary kinetic data of the isothermal decomposition of samples 1 and 3 of zinc hydroxy azide resemble the results for sample 2 presented in figure 1.

(i) The kinetics are deceleratory throughout the run at all temperatures.

(ii) The maximum value of a that could be recorded was only 0·75 above which the sample exploded.

(iii) The initial period of decomposition is described by the unimolecular decay law (figure 2) and the later period by the contracting volume law (figure 3). The activation energies corresponding to these two regions for sample 2 are 42 ± 2 and 22 ± 2 kcal mol⁻¹ respectively.

A few differences in the kinetic behaviour were, however, noticed in the case of sample 3 :

(i) The initial region of decomposition is fitted well by the unimolecular decay law (figure 4) with an activation energy of 33 ± 2 kcal mol⁻¹, followed by a region
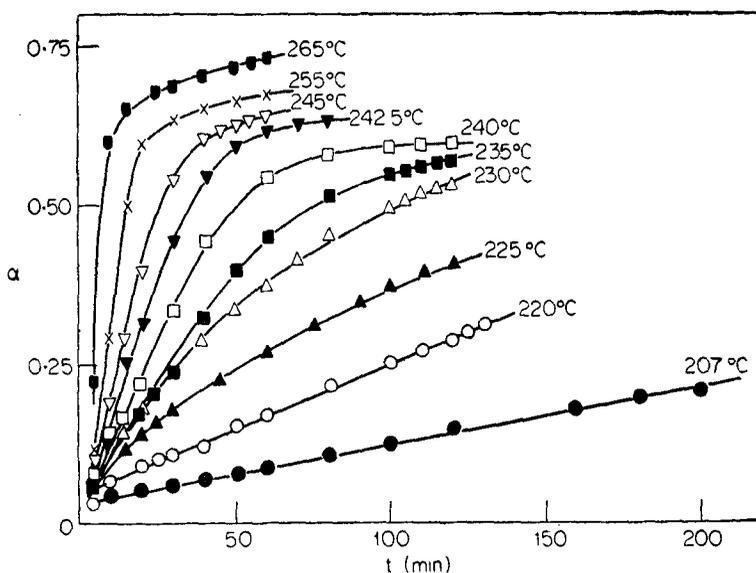

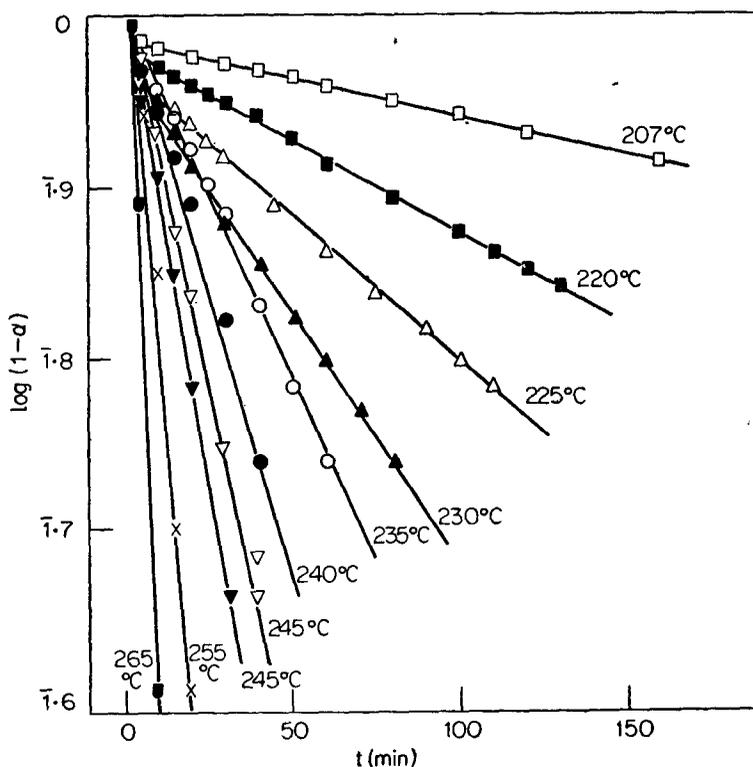**Figure 1.** Thermal decomposition of zinc hydroxy azide, sample 2. Fractional decomposition as a function of time.

Figure 2. The initial period of decomposition of sample 2, described by unimolecular decay law : $\log (1 - a) = - k_1 t$.
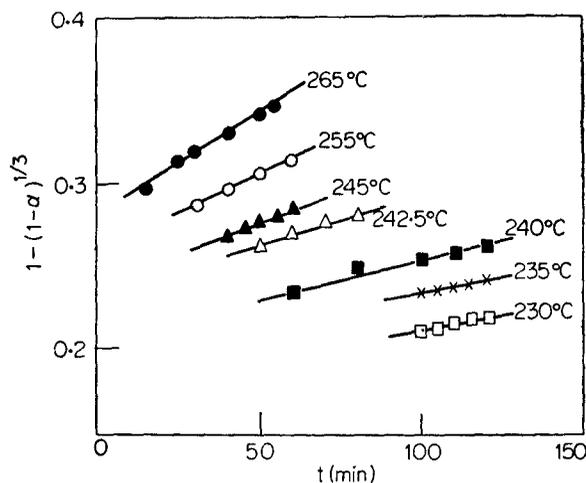

Figure 3. The contracting cube plot of decomposition of sample 2.

where both unimolecular as well as contracting cube equations fit the data equally well (figures 4 and 5), with the same order of energy of activation, i,e., 16 ± 1 kcal mol^{-1}. The final decay reaction is governed by the contracting envelope geometry of the growth of the interface with an activation energy of $16 \cdot 5 \pm 1$ kcal mol^{-1}.
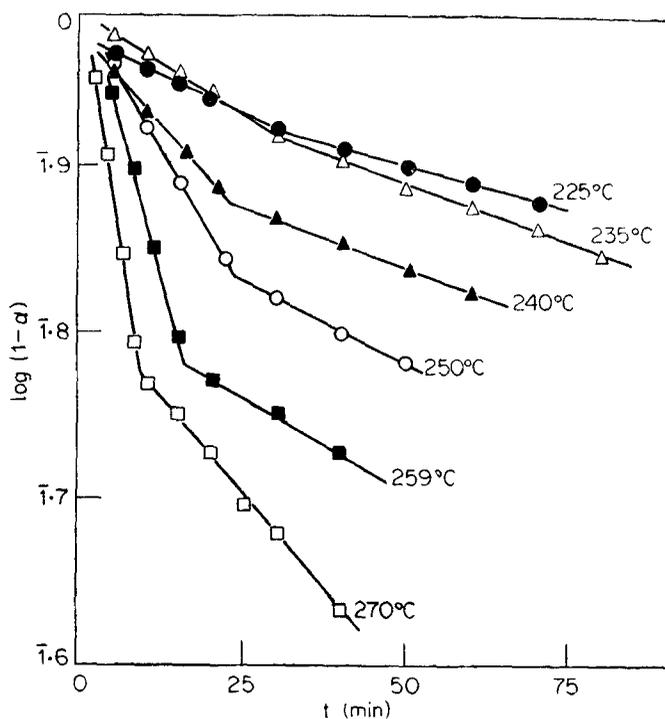
Figure 4. Plot of log $(1 - a)$ versus time for zinc hydroxy azide (aged) sample 3
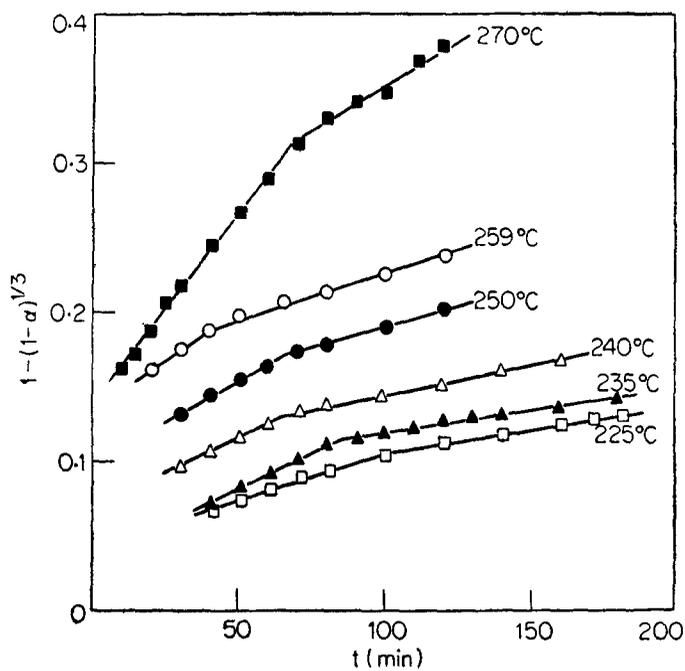

Figure 5. Plot of contracting cube equation for sample 3.

(ii) The degree of decomposition of the aged sample is less by about 30–40% of that obtained for sample 2 at the same temperature and time.

(iii) The thermal decomposition of sample 3, pre-heated for 4 hr at 100° C takes place according to the unimolecular decay law followed by the contracting cube equation, with rates higher than those of the aged sample and with lower activation energy. The intermediate stage observed in sample 2 disappears on pre-heating the sample. The a, t data of the pre-heated sample are compared with those of the untreated sample 3 and are plotted in figure 6.

4. Discussion

The shape of $a - t$ plots for the thermal decomposition of the three samples is amenable to interpretation by either of the following topokinetic models.

(i) Nucleation may be instantaneous on the entire surface of all particles at the commencement of the decomposition.

(ii) Each individual particle may be nucleated with na equal probability and nucleation will be followed by a very rapid surface growth. Once all the particles are covered by a thin film of the nuclei, as expected in both the models, a slow growth of the reaction interface into the bulk of the crystallites should be the obvious process. If on the other hand the penetration into the bulk of the crystal was also a rapid process, the decomposition would have led to a detonation. It is therefore only to be expected that the initial reaction must be described by first order kinetics (Jacobs and Tompkins 1955; Young 1966) as

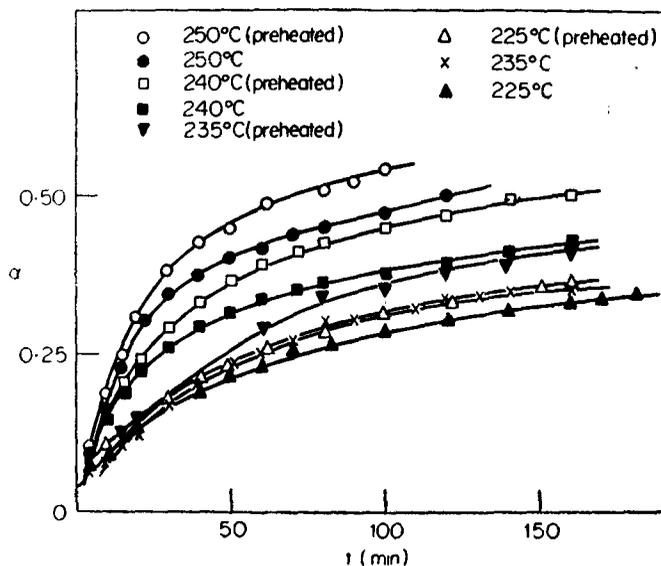$$\log (1 - a) = a - \frac{k_1 t}{2 \cdot 303}, \tag{3}$$

Figure 6. Thermal decomposition of zinc hydroxy azide, sample 3, pre-heated at 100° C for 4 hr.

so that log $(1 - a)$ must be a linear function of t. The essential form of the above equation remains independent of the geometries of the particles.

The rate constants of decomposition of sample 2 are higher than those of samples 1 and 3. Samples 1 and 3 could be compared because both are aged for about equal period of 8–10 months. Sample 1 was obtained by evaporation of a dilute aqueous solution of zinc azide whereas sample 3 was prepared by hydrolysis of zinc azide obtained from its dihydrate. The process of dehydration and hydrolysis is likely to create more defects in the structure of the resulting solid. The greater the number of defects, the greater will be the reactivity. Also, the higher azide content of sample 3 (N = 38%) as compared with sample 1 (N = 29·8%) is responsible for the greater thermal reactivity of the former.

4.1. *Effect of ageing*

Several azides such as those of barium (Yoganarasimhan 1968), calcium (Tompkins and Young 1965) and lead (Jach 1963), silver oxalate (Finch *et al* 1954), mercury fulminate (Bartlett *et al* 1956), etc., are known to show strong effects of ageing on the kinetics of thermal decomposition. The ageing could be accompanied by annealing of potential nucleation sites on the surface as in the case of barium and calcium azides, or deactivation of nucleation sites as in the case of mercury fulminate or the growth of compact nuclei similar to that in silver oxalate. Annealing will have the effect of stabilising the crystallites and preventing a fracture of the crystallites during a growth process. Such a phenomenon has been observed in the case of aged crystals of potassium permanganate (Erofeev 1961).

The effect of ageing on the thermal decomposition of lead azide will be more relevant in this discussion because lead azide is known to form a series of basic lead azides and also to develop films of basic lead carbonates on the surface during ageing (Cook *et al* 1963; Feitknecht and Sahli 1957). An evolution of traces of carbon dioxide and hydrazoic acid during the early stages of decomposition of lead azide has been noticed. This evolution is reported to considerably complicate the kinetics of subsequent decomposition. Since zinc hydroxy azide can also exist in a wide range of non-stoichiometry, and oxide or carbonate layer can be formed on the surface of the particles subject to the thermochemical requirements of the partial pressures of carbon dioxide and water vapour, a lower rate of initial decomposition can be expected in the aged sample. The observation of an intermediate region which is fitted equally well by both exponential decay law and the contracting volume law in the kinetic analysis can be traced to the layer structure of zinc hydroxy azides. The pure zinc hydroxy azide, $Zn(OH)N_3$ is reported (Feitknecht and Zschaler 1957) to have C–19 structure with metal atoms above one another, and the azides and hydroxides forming alternate layers. $Zn(OH)_{2-x}(N_3)_x$ is also reported to have a C–19 structure with OH and N_3 distributed ta..istically, the distribution density of any particular ion in a given layer depending upon the value of x. Since sample 3 has more azide content than required for attaining distinct azide and hydroxide layers, it can be safely assumed that the excess azide groups will infiltrate into the hydroxy layers. So, initially nucleation will be preferentially taking place at azide layers resulting

in a fast reaction. When the azide layers have been fully nucleated and the inward growth of the interface has commenced, the nucleation at the azide centres in the hydroxy layer also starts giving rise to an intermediate exponential nucleation region. The rate of nucleation in this second stage is smaller because the thermal excitation of the azide ions in the pure azide layer will be governed by different energetics than when the azide ions are distributed among the OH ions. Thus, in the transition stage of decomposition, during which growth of nuclei in the azide layers and nucleation at reactive sites in the hydroxy layers take place simul- taneously, both the contracting cube and the exponential decay rate equations are equally applicable. When a sufficient number of growth nuclei produced upto the transition stage have attained a critical size to coalesce with one another a contracting volume kinetics of the growth of the interface sets in. This model of nucleation has a supporting evidence in the results of thermal decomposition of the sample 3, pre-heated at 100° C for about 4 hr. The decomposition of pre- heated samples obeys unimolecular law followed by the contracting cube law without any intermediate stage. During pre-heating, the annealed out active sites on the aged sample are regenerated, and the nucleation during thermal decomposition is very fast as in the fresh sample.

Acknowledgements

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