Photo-decomposition of zinc hydroxy azide

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Abstract. The irradiation of zinc hydroxy azide $Zn(OH)_{2-x}(N_3)_x$, fresh and aged both, with a full output from a high pressure mercury arc results in a spontaneous evolution of nitrogen. The photodecomposition has been carried out as a function of intensity, wavelength of light and temperature. The rate of photolysis on prolonged irradiation for about 1000 minutes continuously decreases to a steady state value. Based upon the assumption of exciton formation and their getting trapped at special sites, a kinetic scheme is worked out which leads to linear dependence of the rate on number of special sites and intensity of radiation. Filters have been used to identify the regions of wavelengths to which the compound is sensitive. The rates of photolysis of the aged sample at all intensities are found to be lower than the corresponding rates for the fresh sample.

Keywords. Photolysis ; zinc hydroxy azide ; kinetics of decomposition.

1. Introduction

In a series of investigations on zinc azide, $Zn(N_3)_2$ (Yoganarasimhan and Jain 1969; Yoganarasimhan and Sood 1973, 1974; Winkler and Krischner 1975), one of the major difficulties frequently encountered was the hydrolysis of the compound while handling it. The hydrolysis of zinc azide on prolonged exposure to laboratory atmosphere or to controlled humidity resulted in its change to non-stoichiometric zinc hydroxy azide, $Zn(OH)_{2-x}(N_3)_x$. Earlier, hydroxy azides of zinc (Feitknecht and Zschaler 1957) of the formulae $Zn(OH)N_3$; $Zn(OH)_{2-x}(N_3)_x$ and $Zn(OH)_3 . Zn_2N_3$ have been prepared and characterised. Detailed structural analysis of basic zinc azide has not been carried out so far, except a somewhat incomplete study reported by Feitknecht and Zschaler (1957). We were not able to prepare zinc hydroxy azide conforming to the exact stoichiometry $Zn(OH)N_3$. Probably this handicap is a feature common to all basic azides. The values of x in two samples of $Zn(OH)_{2-x}(N_3)_x$ studied by us are 0·86 and 1·16. The kinetics of decomposition of the basic form of zinc azide have however not been reported so far and the mechanism of decomposition is unknown. In continuation

of the work done on normal zinc azide, we report in this paper measurements of the kinetics of photodecomposition of zinc hydroxy azide samples prepared in two different ways. In view of the possibility of the hydroxy azide undergoing dehydration during prolonged storage over P_2O_5, the effect of ageing on kinetics of its photolysis has also been reported now. The rates of photolysis of the aged sample at all intensities are lower than the corresponding rates of the fresh sample. This observation has been related to the effect of atmospheric carbon dioxide on several basic azides (Cook *et al* 1963).

An attempt has been made through the use of filters to identify the regions of wavelengths which cause photolytic decomposition. In the absence of supporting evidence through photoconductivity measurements and low-temperature resolution of exciton levels, complete mechanism of photodecomposition of the compound is difficult to envisage. A scheme of reactions as applied earlier to the photo-decomposition of normal zinc azide has, however, been useful to explain the results of photolysis of zinc hydroxy azide. The striking similarity of the time-, intensity- and temperature-dependence of the rate of photolysis of zinc hydroxy azide with that of normal zinc azide suggests the possibility of dehydration of the basic azide preceding the actual decomposition

$$2 \, Zn(OH)_{2-x}(N_3)_x \rightarrow (2-x)ZnO \, . \, xZn(N_3)_2 \, . + (2-x) \, H_2O.$$

The compounds similar to $xZn(N_3)_2 . yZnO$ are known with lead azide system and other basic azides (Cook *et al* 1963). Both Zn and ZnO can be the products of decomposition. The role of ZnO is, however, not known and the matter requires further study.

2. Experimental

The samples of zinc hydroxy azide were prepared in the following two ways.

Sample 1. The zinc azide dihydrate $Zn(N_3)_2 . 2H_2O$ crystals, prepared by an adaptation of Brauer's (Brauer 1963) method for $Ba(N_3)_2$, were dehydrated over P_2O_5 and the resulting normal zinc azide exposed to moist atmosphere (relative humidity > 80%) for several days and then ground to the size − 200 + 250 mesh (B.S.S.). The analysis of nitrogen and zinc contents of the sample, done after $1\frac{1}{2}$ months of its preparation, gave N = 36%, Zn = 51·2% and OH, etc. = 12·8%. This sample shall be referred to as the fresh sample.

Sample 2. A part of the sample 1 was aged over P_2O_5 in vacuum for about 10 months to determine the effect of ageing on its subsequent decomposition. The analysis of the sample at its various ages showed a gradual increase in nitrogen content from 36% to a constant value of approximately 38%. This sample has been referred to as the aged one.

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

The azide was contained in a transparent silica cell with a flat window, connected to a conventional vacuum line. The temperature of the salt was measured with a calibrated copper-constantan thermocouple. The intensity of the irradiation from the high pressure mercury arc (HPK 125 W, Philips) was altered by varying

the distance of the lamp from the photolysis cell. The lamp was calibrated actino-metrically and since its intensity distribution was known, the number of quanta received by the azide, therefore, could be calculated. The filters used to isolate the photolytically active regions of the light source are described later in this paper. The diffuse reflectance spectrum of the compound was recorded with a SP 700 spectrophotometer in the 200–600 nm region with MgO as reference.

3. Results

As in the case of the normal zinc azide (Yoganarasimhan and Sood 1974), irradiation of samples 1 and 2 of zinc hydroxy azide with a full output from the high pressure mercury arc results in a spontaneous evolution of nitrogen. The photochemical decomposition as a function of intensity, wavelength and tempe-rature was carried out in both samples. The pressure-time data of decompo-sition of all the samples could be fitted best only in the rate equation of the form $P = S \sqrt{t}$ where S is a constant including the intensity term. The results of decomposition of the fresh (sample 1) and the aged (sample 2) compound are described below.

Sample 1. (i) The rate of evolution of N_2 at constant temperature and intensity decreases with time. The $p-t$ data of photodecomposition at constant temperature (35° C) and eight different intensities (ranging from $2 \cdot 4 \times 10^{15}$ to $18 \cdot 1 \times 10^{15}$ quanta/sec/cm²) are plotted in figure 1 (*a*). The pressure of nitrogen built up at time t varies directly as $\sqrt{t}$ at all intensities as shown in figure 1 (b). On plotting the values of the constant S against the intensity, a straight line is obtained. Thus the rate of photolysis at constant temperature at equal intervals of time varies linearly with intensity.
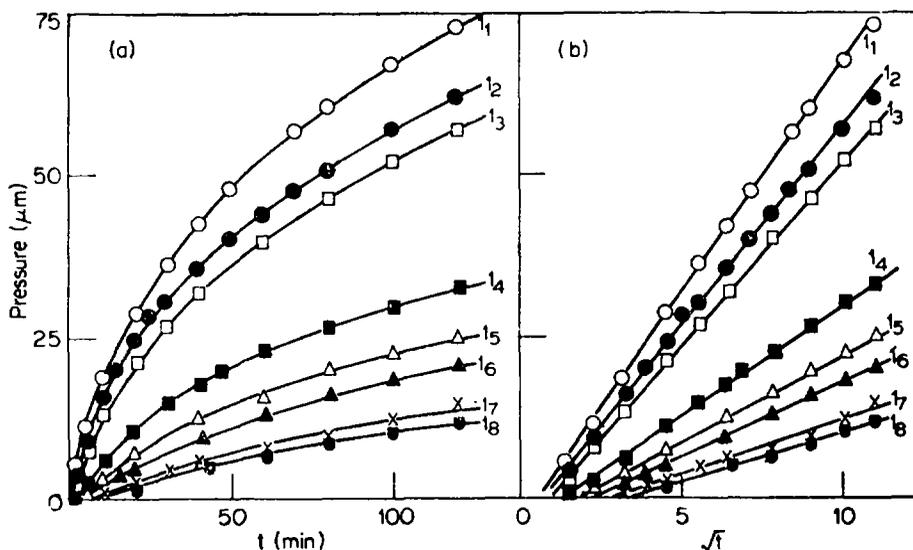

Figure 1. (a) The pressure-time plots of photolysis of zinc hydroxy azide at con-stant temperature (35° C) and different intensities, (b) Pressure versus $\sqrt{t}$. $I \times 10^{-15} = 18 \cdot 1$, $16 \cdot 3$, $14 \cdot 4$, $8 \cdot 1$, $5 \cdot 8$, $4 \cdot 3$, $3 \cdot 0$, $2 \cdot 4$ photons/cm²/sec for I_1 to I_8 respectively.

(ii) The kinetics of photolysis at constant intensity in the temperature range 45° to 5° C also follow a parabolic rate law. The energy of activation is found to be 0·8 Kcal mol^{-1}.

(iii) The dark-reaction rate constant is independent of intensity. This is inferred from the plots of the normalised dark-reaction pressure values $1 - P/P_\infty$ versus $\sqrt{t}$, where P_∞ is the total pressure built up during dark reaction (figure 2).

(iv) The rate of photolysis on prolonged irradiation of the sample extending upto about 900 min decreases progressively with time, very sharply upto about 200 min and attaining a steady value thereafter (figure 3).

Sample 2. (i) The sample was photodecomposed at the same temperatures and intensities as sample 1. The rate law obeyed is also the same. The rate of photodecomposition of this sample is, however, lower than that of the fresh sample at the corresponding intensities and temperatures.

(ii) The Arrhenius plot in the temperature range −15° to +45° C gives the activation energy of photodecomposition equal to 1·2 Kcal mol^{-1}.

(iii) The dark-reaction rate constants are intensity-independent, as in the case of fresh sample.

3.1. *Photolysis through filters*

In order to find out the wavelengths which are photolytically active, further experiments on photolysis were carried out making use of the following cut-off filters.

(i) Perspex filter (Chance OY10) which absorbs all radiations with $\lambda < 380$ nm. Interposition of this filter between the sample and the source of light reduces the rate of decomposition to almost zero.

(ii) Filter H556 (Hilger–Watts) which transmits only between 300 nm and 400 nm. This filter has a sharp maximum transmission of 68% at 365 nm (figure 4a).
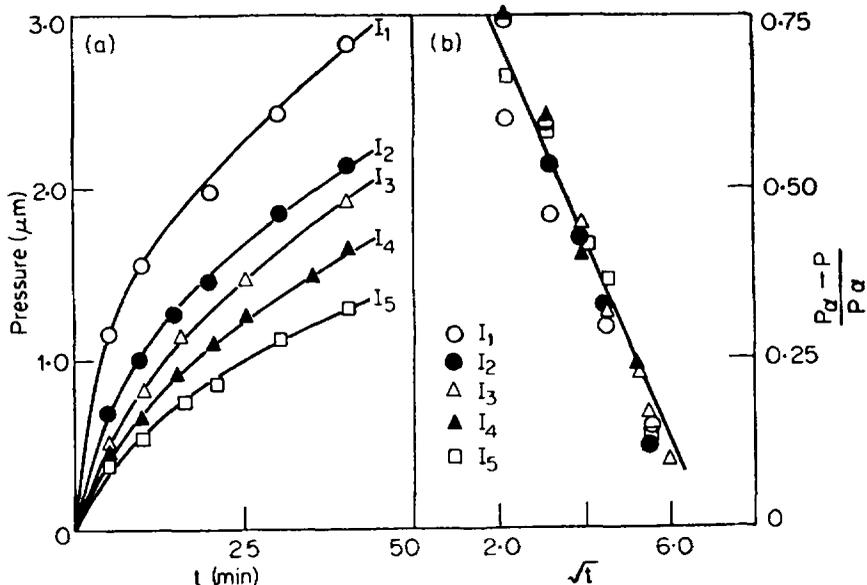

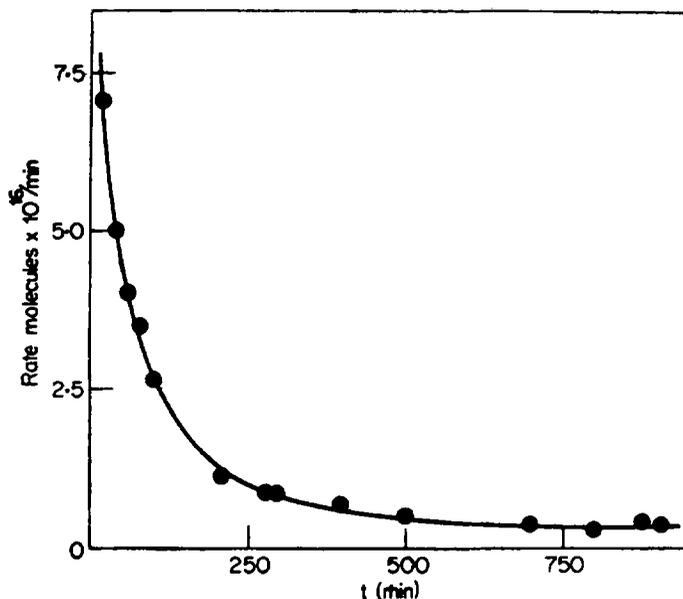Figure 2.   (a) Dark-reaction pressure versus time.   (b) Normalised dark-reaction pressures as a function of $\sqrt{t}$.

Figure 3. Prolonged photolysis of zinc hydroxy azide. Rate expressed in molecules, × 10^{16}/min as function of time.

(iii) Benzene filter : Pure benzene (free from thiophene and moisture) filled in a quartz cell completely absorbs $\lambda < 280$ nm and is transparent to the region $\lambda > 280$ nm with a maximum transmission of about 50%. The absorption profile of the filter taken after several exposures for different times (minutes) is shown in figure 4b. After 100 minutes of exposure the transmission falls from 50% to 30%. Obviously the intensity of light reaching the sample through the filter will not remain constant as the photolysis of the sample goes on. However, our interest was to find out, at least qualitatively, whether any photodecomposition of zinc hydroxy azide was brought about by wavelengths greater than 280 nm. Due to lack of suitable ultraviolet cut-off filters, a circular quartz cell with a path of 1 cm filled with pure benzene was improvised as the required filter.

The rate of photolysis through the filters (ii) and (iii) is much lower than the rate of decomposition by the unfiltered light at the same temperature (figure 5).

4. Discussion

Although no accurate data on the absorption spectrum of zinc hydroxy azide are available, it is evident from reflectance measurements (figure 6) that strong absorption commences at about 220 nm and remains constant before it tails off sharply at about 260 nm. Consequently, radiation of wavelength $253 \cdot 7$ nm will be absorbed within the first lattice absorption band. The existence of a high rate of photolysis of the compound when irradiated with high pressure lamp shows that wavelengths longer than $253 \cdot 7$ nm can be photolytically active. This func-
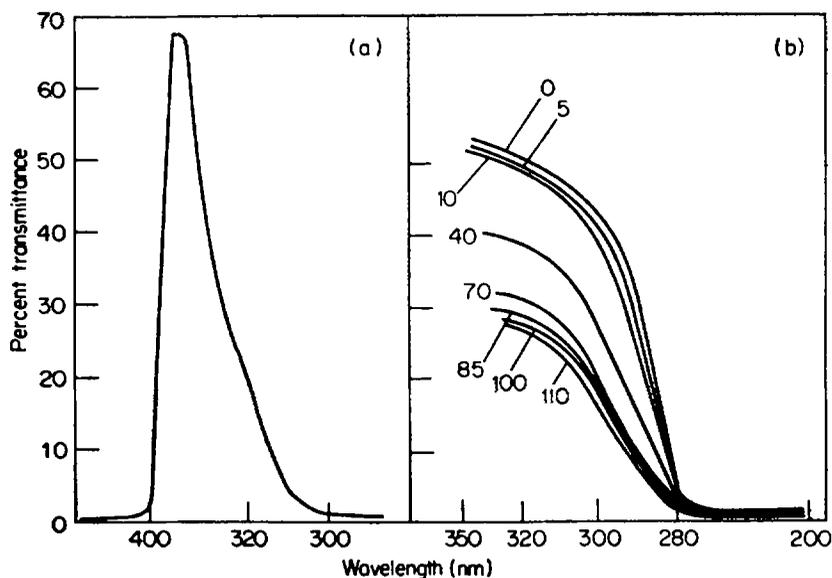
Figure 4. Absorption profile of filters (a) filter H 556 ; (b) benzene filter. Decrease in transmittance with time of exposure of benzene filter is shown. The time (minutes) is indicated with absorption profile.
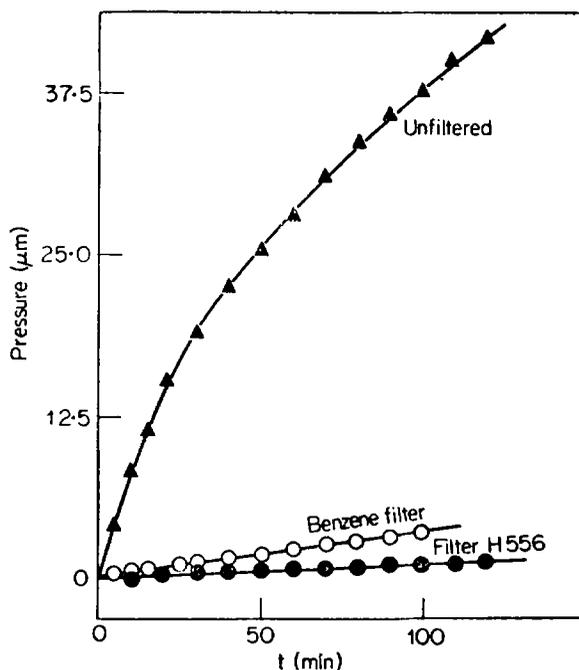

Figure 5. Photolysis of zinc hydroxy azide with and without filters.

tion is limited to $\lambda < 330$ nm, because an introduction of a Perspex filter (Chance OY10) causes the rate to fall to zero. High transparency of zinc hydroxy azide to the ultra-violet radiation beyond 260 nm and low proportion of short wavelengths in the emission spectrum of the light source negate the possibility of band-
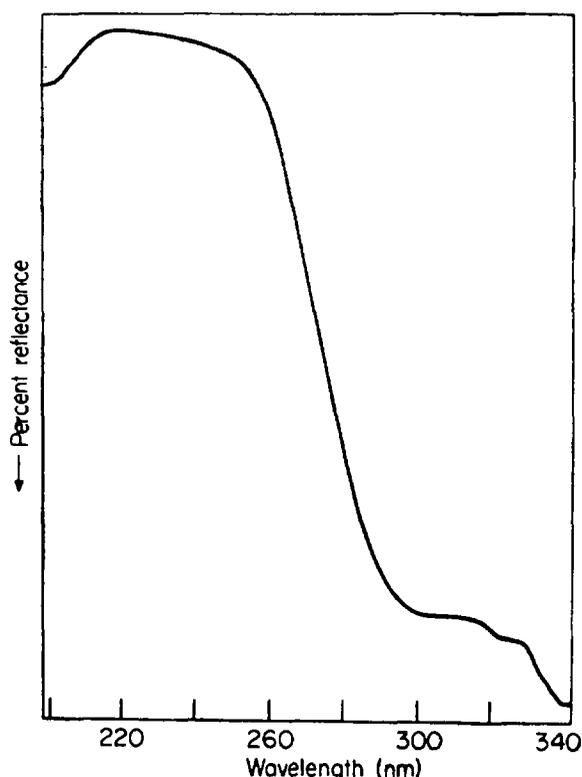
Figure 6. Diffuse reflectance spectra of zinc hydroxy azide.

to-band transition of electron. Therefore, the primary process in the photolysis of zinc hydroxy azide is expected to be the formation of an exciton. The dependence of rate of photolysis on time, intensity and wavelength can be explained on the basis of exciton formation.

4.1. *Time-dependence of rate*

From the parabolic pressure-time plots (figure 1a), the rate equation for the photodecomposition can be inferred as

$$dP/dt = a/p, \tag{1}$$

where a is a constant which includes a term of intensity of radiation. With boundary conditions $P = 0$ at $t = 0$,

$$P = (2at)^{1/2} = S \sqrt{t}, \tag{2}$$

where $S = (2a)^{1/2}$. The plots of P versus $\sqrt{t}$ at all intensities are straight lines (figure 1b). By plotting S versus I, the intensity of radiation, S is found to be a linear function of intensity. Therefore, $S = \sqrt{2a} = b \cdot I$ and the rate equation (1) reduces to

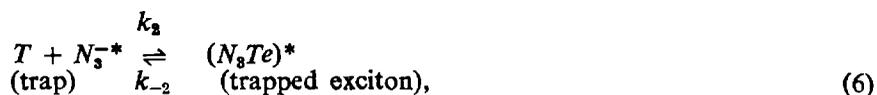$$dP/dt = b \cdot I/\sqrt{t}. \tag{3}$$

The decreasing rate at constant intensity could be explained only if the nature of 'dark rate' measured immediately after the light source is removed, is clearly understood. Any dark reaction that is observed is the result of the 'light reaction' that has already taken place and the evolution of N_2 during the dark reaction is simply escape of the gas accumulated within the azide lattice and at the reaction interface. The accumulation of nitrogen in the interior of the solid—its amount depending upon the intensity of radiation—results in a high pressure gradient between the reaction interface and the surface. The diffusion of N_2 under such pressure gradients shows up as intensity-dependent dark rate (figure 2a). The normalised dark-reaction pressure values plotted against $\sqrt{t}$ give the dark-reaction-rate constants independent of intensity (figure 2b). This is found to be the case with barium azide (Yoganarasimhan 1968) and zinc azide (Yoganarasimhan and Sood 1973). Yoganarasimhan et al (1974) tried to explain the dependence of rate of photolysis of zinc azide on $1/\sqrt{t}$ employing a model which involves formation and trapping of excitons at special sites with consequent reaction of the trapped exciton with adjacent azide group resulting in molecular nitrogen which diffuses towards the surface. Their model yields a solution of the diffusion equation for the rate of decomposition as

$$dP/dt = N_0\, I \sqrt{D/\pi}\; 1/\sqrt{t}\,, \tag{4}$$

where N_0 is the number of azide species at special positions at the beginning of photolysis and I is the intensity. The fall in the observed rate of photolysis may probably be attributed to the inhibition of evolution of nitrogen at the surface due to slow diffusion in the bulk.

4.2. Intensity-dependence

Following the methodology of Jacobs et al (1959), it can be proposed that for the case of zinc hydroxy azaide as for zinc azide (Yoganarasimhan and Sood 1973) the trapped excitons, during their lifetime, may dissociate into mobile holes and electrons which should ultimately recombine at traps. Alternatively, a trapped exciton, if favourably disposed can interact with an adjacent azide ion, as mentioned above, resulting in chemical reaction with consequent evolution of nitrogen. The traps can be only special sites notably near dislocations where selection rules are relaxed. These possibilities are summarised as :

$$N_3^- + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_3^{-*}\,, \tag{5}$$

$$\begin{array}{l} T + N_3^{-*} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (N_3Te)^* \\ \text{(trap)} \qquad\qquad \text{(trapped exciton)}, \end{array} \tag{6}$$

$$[N_3Te]^* + N_3^- \overset{k_3}{\rightarrow} 3N_2, \tag{7}$$

$$[N_3Te]^* \rightleftharpoons N_3 + T + e. \tag{8}$$

By applying the steady-state hypothesis with the assumptions that the concentration of $[NTe]^*$ is maintained essentially by the reaction (6) and the concentration

of N_3^- is constant (the degree of photo-decomposition is small), the rate expression for evolution of nitrogen can be written as

$$dN_2/dt = \frac{T \cdot k_1 \cdot k_2 \cdot k_3 \cdot I}{(k_{-2} + k_3)(k_{-1} + k_2)} \cdot \qquad (9)$$

The rate is, therefore, proportional to the number of special sites and the intensity of photolytic radiation. A progressive decrease in the number of special sites as the reaction continues will lead to diminishing number of trapped excitons and consequently a sharp lowering of the rates in the initial stages. The decrease in rate with eventual attainment of a steady value in the later stages of decomposition will be controlled largely by inhibited diffusion of the gaseous product. The combined effect of these two factors is exhibited by a continuous fall of the rate of photolysis to a non-zero minimum value during prolonged irradiation of the compound (figure 3).

4.3. *Wavelength dependence*

The rate of photolysis through the filter OY10 is zero. This suggests that $\lambda > 330$ nm are photochemically inactive in zinc hydroxy azide. Since $\lambda = 365$ nm, transmitted maximum by filter H 556, is not photolytically active, the observed rate of decomposition under this filter must be due to the activity of $\lambda < 330$ nm. Even though the average transmission of the benzene filter is only about 40% in the region 290–350 nm, the appreciable rate of photolysis (figure 5) suggests that the wavelengths in the region 280–330 nm could also be photolytically effective for zinc hydroxy azide.

The pressure-time curves of photolysis through both the filters (figure 7) show an acceleratory period after an initial spurt of gas. This particular behaviour is very similar to the one shown by unfiltered photolysis of barium azide (Yoganarasimhan 1968) obtained from 1·5 monohydrate. One of the mechanisms suggested invokes the concept of deep surface traps for the mobile excitons in the azide lattice. The greater the concentration of surface imperfections and deeper the surface levels, the less chance of an interaction between two excitons trapped or otherwise. In the initial stages, therefore, the possibility of bimole-
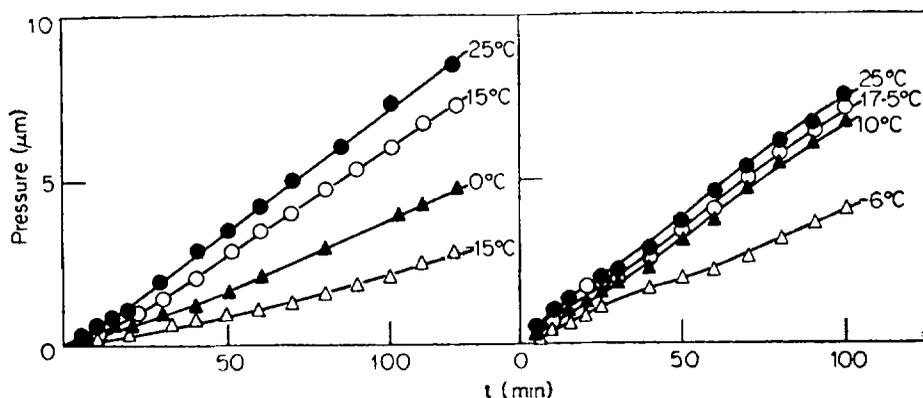

**Figure 7.** The pressure-time plots of photolysis through filters.

cular decomposition of excitons is less than what it would be after all the deep traps are filled. In the present case, the filters cut off most of the more actinic wavelengths and a very small intensity of radiation reaches the sample, with much less penetration into the interior of the solid. This results, in the initial stage, in a predominantly surface reaction with a rate which accelerates when all the available deep surface traps are filled. The unfiltered photolysis proceeds with too high a rate, even at low intensities, to allow any deactivation process to be observable.

4.4. *Effect of ageing*

The rates of photolysis of the aged sample are found to be lower than those of the fresh sample at the corresponding temperatures and intensities. The effect can be attributed to

(i) Annealing of the surface singularities and lattice defects (which are always in excess of thermodynamic equilibrium when the sample is freshly prepared) and a consequent decrease in the number of traps available for excitons.

(ii) Contamination of the compound with the carbonate because basic azides can react with atmospheric carbon dioxide during storage as

$$2M(OH)N_3 + H_2O + CO_2 \rightleftharpoons M(OH)N_3 \cdot MCO_3 + HN_3.$$
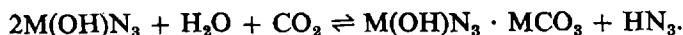
The carbonate coating on the surface will increase the extinction coefficient of irradiating light by itself absorbing some of it. The appearance of a small peak around $870 \, cm^{-1}$ due to carbonate in the infrared spectrum of the aged sample supports the argument. Moreover, formation of some ZnO on the surface as a result of dehydration of the hydroxy azide during storage over P_2O_5 is a distinct possibility. The zinc oxide will also contribute to the deactivation process.

4.5. *Quantum yield*

The calculated quantum yield is the average of the contributions of the different wavelengths in the actinic ultraviolet region of the source of light, viz. 248 $\langle \lambda \rangle$ $< 365 \cdot 5 \, nm$, the average intensity of which, calculated from the spectral distribution of the light source, is about 17%. By analogy with Jacobs and Tompkin's (1952) observation on KN_3, it has been assumed that 20% of the light is lost by reflection and scattering, for it is extremely difficult to measure the reflectivity of the surface of the zinc hydroxy azide sample. With these approximations, the quantum yield of photolysis was calculated from the results of prolonged photolysis of the sample. Its value after 10 minutes of the start of the reaction was about $1 \cdot 8 \times 10^{-1}$. The continuously decreasing quantum efficiency reached a steady-state value of $6 \cdot 5 \times 10^{-3}$ after about 500 minutes of photolysis. The quantum yield of decomposition under the filter H 556 was found to be of the order of 4×10^{-3} after about hundred minutes of irradiation.

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