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Photolysis of Zinc Azide in the Solid State*

S. R. YOGANARASIMHAN AND R. K. SOOD

Department of Chemistry, Indian Institute of Technology, New Delhi 110029, India

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The photolysis of anhydrous zinc azide prepared by (1) dehydration of $Zn(N_3)_2 \cdot 2H_2O$ and (2) precipitation by acetone from aqueous solution, under the action of high pressure mercury arc is reported here. The pressure of nitrogen developed during photolysis under steady-state conditions at constant intensity is a linear function of $t^{1/2}$ in both the samples. The rate of photolysis is a linear function of intensity at constant temperature. A detailed analysis of the dark rate suggests that the dependence on $t^{1/2}$ should be due to the diffusion of nitrogen from the reaction site to the surface of the solid azide. An appropriate mathematical analysis is presented. The linear dependence of the rate of photolysis on the intensity of irradiation is interpreted in terms of the reaction of a trapped exciton with an adjacent azide ion. Absence of any detectable photoconduction in the wavelength range of the irradiating radiation suggests that excitons are the most probable reactive species. The sample of zinc azide obtained by the first method decomposes faster than the other under identical conditions, and has a slightly lower energy of activation of 1.4 kcal/mole compared to 1.75 kcal/mole for the second. These differences are discussed in terms of the defect concentrations of the two azide samples.

There have been several investigations of the decomposition of metal azides under the action of photons and heat. Most of these studies are on alkali metal azides (*1–3*), alkaline earth azides particularly barium azide (*1*, *4*, *5*) and some heavy metal azides such as lead azide (*6*) and copper azide (*7*). Photolysis of these azides are generally interpreted in terms of a mechanism originally proposed by Jacobs, Tompkins, and Young (*8*) for barium azide with the necessary modifications. The dependence of the rate of photolysis on a function of the intensity of the irradiating radiation is indicative of the number of participating radicals in the final stage of decomposition. Several azides failed to show any photoconduction on irradiation at the same wavelength which effects photolysis, suggesting that the primary process of excitation under uv light was the formation of excitons. Further experimentation (*4*) showed that the mechanism of photolysis must be more complex than simple bimolecular decomposition of excitons at traps.

While extensive experimentation has been carried out on the alkali and alkaline earth azides, the azides of the zinc group have completely escaped detailed investigations the reasons probably being that zinc, cadmium, and mercuric azides are highly explosive. Pauling (*9*) suggests that the explosive nature of the azides should be related to the covalent bonding between the metal atom and the azide group. However, a satisfactory correlation between these two parameters has not been found. Our interest is to obtain information on the decomposition of the azides of the zinc group of metals to test the applicability of theories developed for purely ionic azides and to find the mechanism of slow decomposition of these explosive azides. The only attempts in understanding the decomposition of zinc azide has been made by Yoganarasimhan and co-workers (*10–12*).

The results of photodecomposition of anhydrous zinc azide obtained by (1) dehydra-

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* Material taken from the Ph.D. Thesis of R. K. Sood.

tion of $Zn(N_3)_2 \cdot 2H_2O$, and (2) direct precipitation from aqueous solution of zinc azide by the addition of acetone are presented and discussed in this communication. The decomposition studies have been carried out on well aged samples. The two samples are referred to as ZnN_6 I and ZnN_6 II, respectively. The rates of decomposition are discussed in terms of the defect structure of the solid azide.

Materials and Methods

The cell used in the photodecomposition studies consisted of Pyrex glass tube, 2.5 cm diameter and 10 cm length and a B-24 joint at the end. A 3 mm thick optically plane quartz window was sealed on to the top of the cell by means of pycene wax and irradiation of the sample was done through it. The source of irradiation was an ordinary high pressure mercury lamp HPK 125, which has a strong emission at 2537 Å and a number of weaker and stronger components at 3130, 3650, 4047, 4358, 5461, 5770, and 5791 Å. No filters were used to obtain the maximum intensity. Different intensities of irradiation were obtained by varying the distance of the lamp over the specimen. The volume of the closed system, consisting of Mcleod gauge, photolysis cell and traps employed for photolysis was determined to enable the evaluation of the degree of decomposition. The pressure of nitrogen developed during photolysis was measured with the Mcleod gauge.

In a typical photolysis run, 20 mg of the sample were weighed accurately and spread uniformly at the bottom of the cell. The sample was then continuously evacuated for 48 hr at 10^{-6} Torr. The cell was covered with an opaque screen during the warm up period of the lamp which was set at a predetermined distance. The initial dark rate which is the sum of the degassing rate of the sample and the

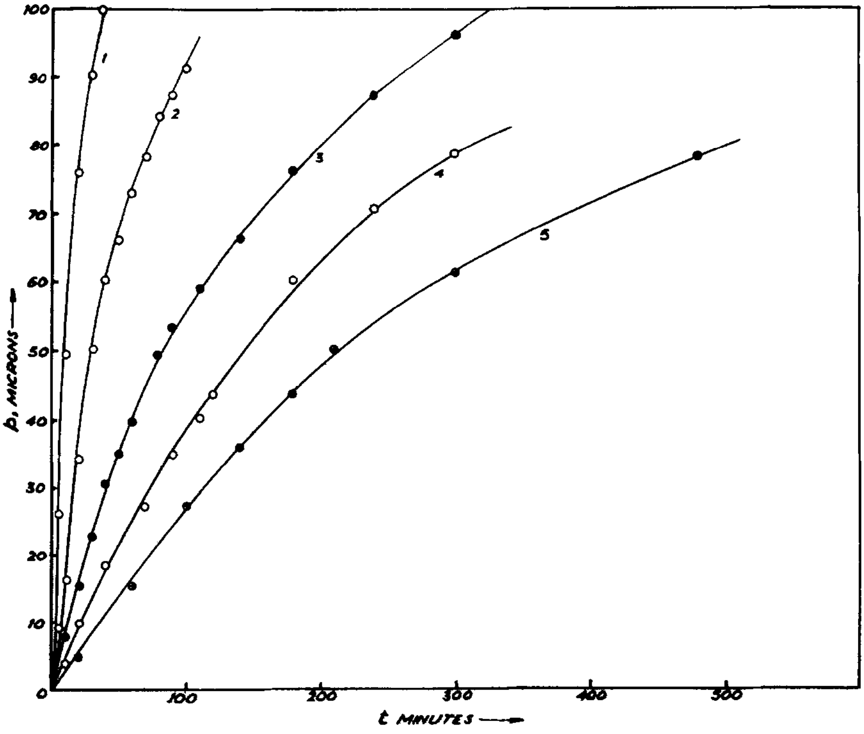

FIG. 1. Pressure of nitrogen developed during the photolysis of ZnN_6 I at different intensities. $T = 298°K$. Intensities are 277.7, 126.8, 64.6, 44.2, and 30.72 arbitrary units, respectively, for curves 1-5.

rate of the thermal decomposition of the sample at that temperature was measured. The accumulated gas was pumped out at the end of determination of dark rate, uv light was then allowed to fall on the sample. Pressure of nitrogen was recorded as a function of time.

The final dark rate was recorded at the end of prolonged photolysis until it became very nearly equal to the initial dark rate. The initial dark rate was deducted from the measured rate of photolysis to get the true rate of photolysis.

Results and Discussion

Irradiation of well aged "fresh" sample of zinc azide with uv light results in the spontaneous evolution of nitrogen. Figures 1 and 2 show the pressure of nitrogen developed in a constant volume system during the photolysis of samples of zinc azide I and II at various intensities. The rate of evolution of nitrogen progressively decreases with time. The degree of decomposition, α, in the case of both the samples at all temperatures and intensities was found to vary as $t^{1/2}$. Figures 3 and 4 show the dependence of α on $t^{1/2}$. The rate equation for the photolysis can therefore be written as

$$d\alpha/dt = a/\alpha, \tag{1}$$

where a is a constant which includes an intensity term. On solving for α we get

$$\alpha = (2at)^{1/2} + \text{constant}.$$

Since

$$\alpha = 0 \text{ at } t = 0, \quad \text{constant} = 0.$$

Therefore,

$$\alpha = (2at)^{1/2}.$$

The dependence of the rate of photolysis on intensity can be determined by plotting $(2a)^{1/2}$ against intensity of irradiation. $(2a)^{1/2}$

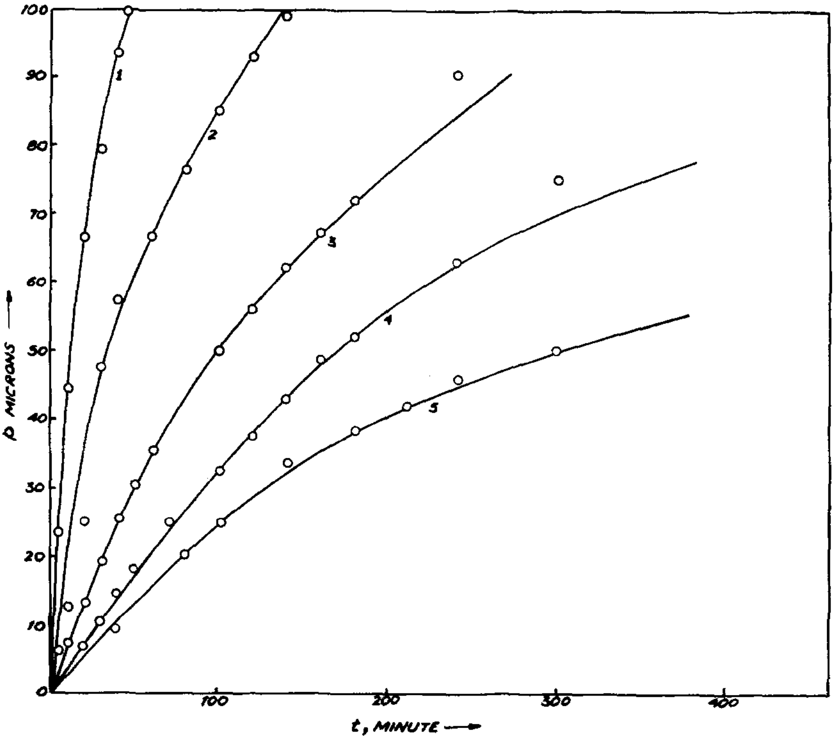

FIG. 2. Pressure of nitrogen developed during the photolysis of ZnN_6 II at different intensities. Temperature and the intensities are the same as in Fig. 1.

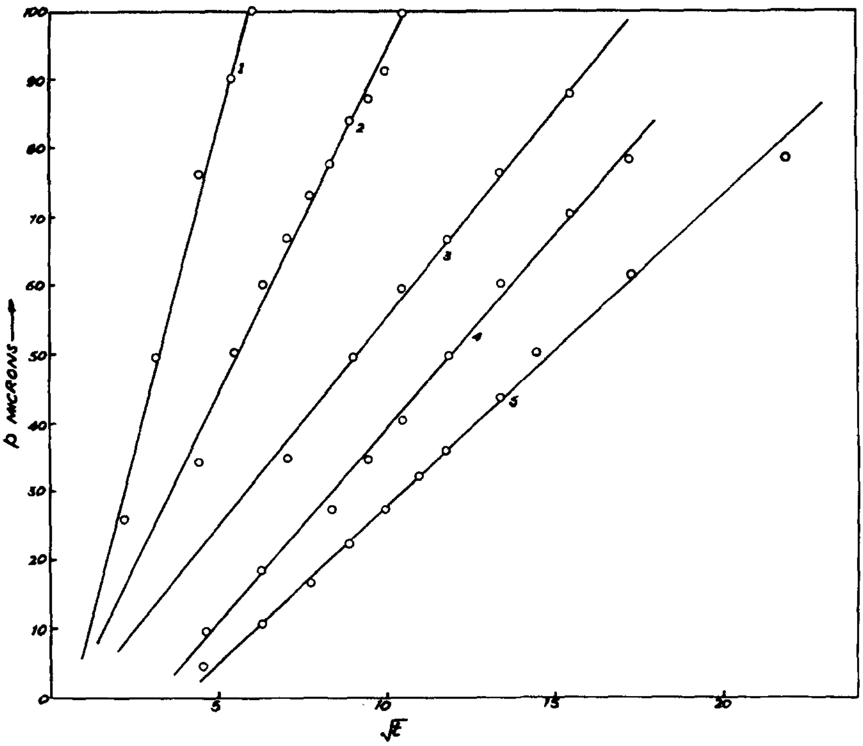

FIG. 3. Parabolic dependence of the degree of decomposition on time in ZnN_6 I.

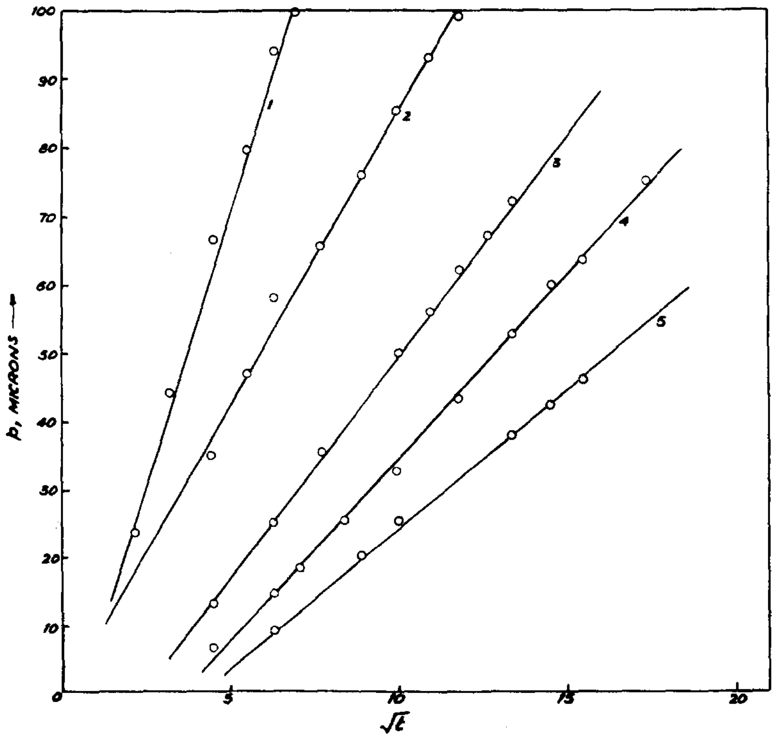

FIG. 4. Parabolic dependence of the degree of decomposition on time in ZnN_6 II.

is experimentally found to be a linear function of intensity. Therefore

$$a = b^2 I^2/2, \quad \text{where } b \text{ is a constant.}$$

On substitution in Eq. (1),

$$d\alpha/dt = bI/2(t)^{1/2}.$$

Therefore the rate of photolysis should be directly proportional to intensity as shown in Fig. 5.

The kinetics of photolysis of the two samples at constant intensity and different temperatures yield an energy of activation of 1.40 and 1.75 kcal/mole for the samples I and II, respectively, in the temperature range $-25°\text{C} < T < +25°\text{C}$ (Fig. 6). The rates of photolysis were found to be higher at liquid nitrogen temperature than expected from Arrhenius equation for both the samples.

Great help in understanding the decrease in the rate of evolution of nitrogen at constant intensity can be derived by a study of the rate of final dark reaction. The final dark rate during the photolysis of barium azide was found to very as (intensity).[2] It was also noticed that the dark rate before attainment of constant rate was much smaller than that after the attainment of constant rate. The dark reaction in the present investigations was also found to be intensity dependent. Any reasonable argument to explain the nature of the dark rate must account for the fact that during the period of dark reaction, intensity of irradiating radiation is zero. Any dark reaction that we observe should be the result of "light reaction" which has already taken place and the evolution of nitrogen during dark reaction should simply be liberation or escape of nitrogen accumulated in the lattice of zinc azide and at the reaction interface. This means that the dark reaction rate must be independent of intensity. The dark reaction is, therefore,

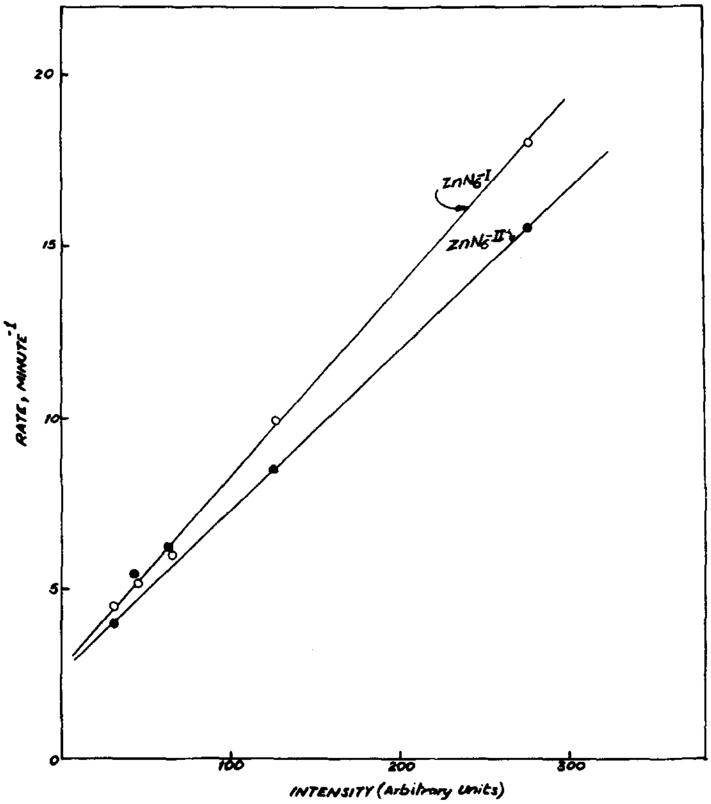

FIG. 5. Dependence of the rate of photolysis on intensity for (i) ZnN_6 I and (ii) ZnN_6 II.

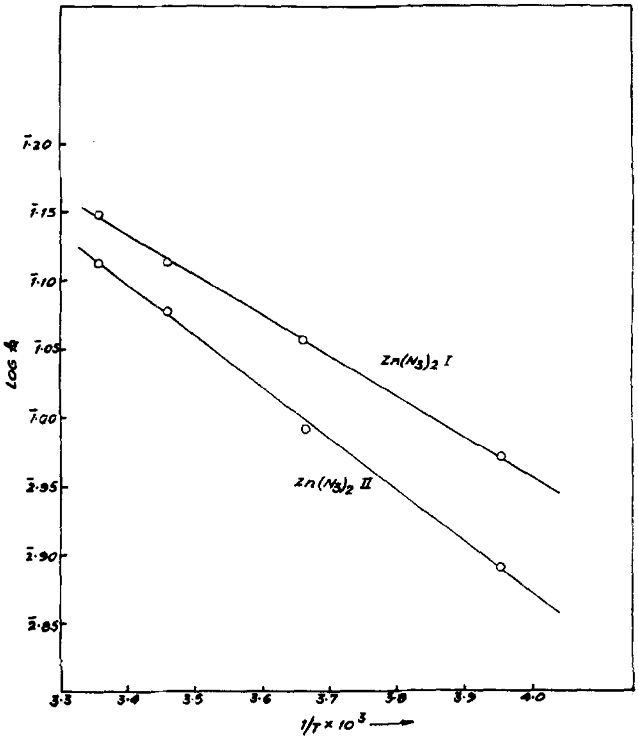

FIG. 6. Arrhenius plot for the photolysis of ZnN_6 I and II at constant intensity.

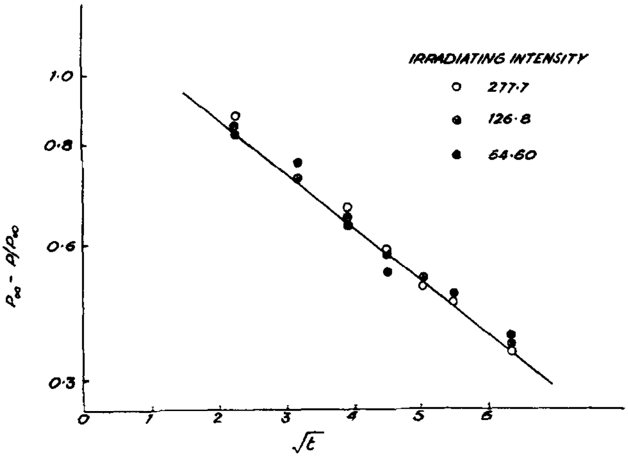

FIG. 7. Normalized dark reaction after the photolysis of ZnN_6 I.

likely to be a diffusion of nitrogen molecules from the interior of the solid to the surface. The amount of nitrogen so accummulated will be directly proportional to the intensity of irradiating radiation. This results in a high pressure gradient between the reaction interface and the surface, and the diffusion of nitrogen under such pressures shows up as intensity dependent dark rate. If the dark reactions are normalized and then plotted against $(t)^{1/2}$, the rate constant must become independent of intensity. Figure 7 shows that it is the case. The conclusion is that diffusion is most likely the phenomenon which inhibits the free movement of nitrogen molecules from the interface to the surface. The inhibition of the evolution of nitrogen at the surface due to a slow diffusion in the bulk is probably responsible for an appreciable part of the observed fall in the rate of photolysis. The second order differential equation,

$$\partial n/\partial t = D(\partial^2 n/\partial x^2), \qquad (2)$$

has been solved with suitable boundary conditions to express the diffussion controlled photolytic rate. The details of the analysis are presented at the end.

The diffuse reflectance spectra of the two samples of zinc azide shows that there is an absorption maximum around 242 nm. The long wavelength tail of this maximum extends upto 330 nm (Fig. 8). On the low wavelength side, the absorption increases sharply after a dip around 230 nm. The samples did not show any appreciable photoconduction in this region. The conclusion is, therefore, that the absorption of radiation of $\lambda > 242$ nm produces excitons.

The excitons thus produced can be mobile within the lattice; they will normally get deactivated by the transfer of phonons to the lattice when they come to rest, and this process is accompanied by the reversion of electrons to the valence band. A second possibility is their interaction during their characteristic lifetime with imperfections in the crystal resulting in their being trapped. The excitons share their electrons, on being trapped, with the imperfections. The trapped excitons may, on receiving appropriate amount of thermal energy, dissociate into mobile holes and electrons which should ultimately recombine at the traps. Alternatively, a trapped exciton, if favourably disposed, can interact with an adjacent azide ion resulting in chemical reaction with consequent evolution of nitrogen. The traps can only be special positions (designated as S) notably near dislocations where the selection rules are relaxed.

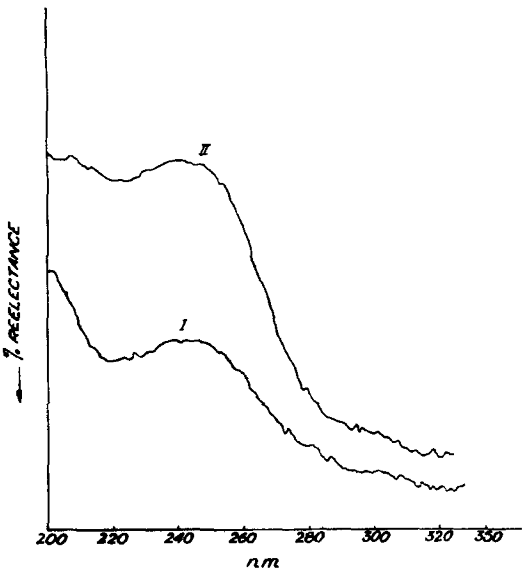

FIG. 8. Diffuse reflectance spectrum of ZnN_6 I and II in the uv region.

$$N_3^- + h\nu \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_3^{-*}. \qquad (3)$$

$$S + N_3^{-*} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} N_3Se^*. \qquad (4)$$

$$N_3Se^* + N_3^- \xrightarrow{k_3} 3N_2. \qquad (5)$$

$$N_3Se^* \rightleftharpoons N_3 + S + e. \qquad (6)$$

Applying steady-state considerations and solving for

$$[N_3^{-*}] = k_1 I/(k_{-1} + k_2). \qquad (7)$$

$$[N_3Se^*] = k_2 S[N_3^{-*}]/(k_{-2} + k_3). \qquad (8)$$

The rate of evolution of nitrogen is given by

$$dN_2/dt = k_3[N_3Se^*][N_3^-]. \qquad (9)$$

Since the degree of decomposition is very small $[N_3^-]$ can be assumed to be constant. We can rewrite equation (9) as

$$\frac{dN_2}{dt} = k_3[N_3Se^*] = \frac{Sk_3k_2k_1I}{(k_{-2}+k_3)(k_{-1}+k_2)}. \tag{10}$$

The rate of photolysis is thus proportional to the number of special sites and the intensity.

The rate of photolysis partly decreases due to the destruction of the traps as the reaction proceeds according to Eq. (5). A progressive decrease in the number of traps with the amount of photolyzed will result in lowering the concentration of N_3Se^*. Since the rate of photolysis is directly proportional to the concentration of N_3Se^*, a lower rate is predicted with the progress of photolysis. However, the dependence of on $t^{1/2}$ cannot be satisfactorily explained by this mechanism. A diffusion controlled rate as discussed earlier has to be invoked to give a quantitative description of the variation of rate with time.

The higher rates in the case of ZnN_6 I should certainly be due to the higher defect concentration introduced in the lattice during the process of grinding and dehydration. Pairs of vacancies of opposite sign separated by a few unit cells, isolated vacancies near edge dislocations, vacancies near the jogs in dislocations are energetically favoured positions, and the decomposition at these places proceeds with less energy. Sample I must be abundant in these defects relative to sample II.

An identification of the special sites at which the reactivity is high is extremely important. The reaction centers are considered in terms of a mosaic boundary consisting of an array of edge dislocations. The decomposition is possible only when both the metal and the azide ions are present in the dislocation cores. With the progress of the decomposition the azide ions are removed and zinc metal is deposited in the sites *S*. It is therefore clear that these sites are destroyed continuously with the progress of decomposition. The filamentary metal deposited in the dislocation core is in the prenuclei form and does not effect the kinetics of decomposition.

The photolysis of the azide will proceed with zero activation energy or with activation energy *E* depending upon the nature of the traps. The traps can be any discontinuity of relevance discussed above. When an exciton is trapped the change in the electronic configuration at the trapping center causes a redistribution of the surrounding lattice with evolution of energy, and if trapping occurs in the region of highest disorder such as grain boundaries or dislocation nets, jogs or kink sites etc. adjacent to an azide ion the reaction between an azide ion and the trapped exciton takes place with zero activation energy. But there is a distinct probability that the excitons are trapped at other imperfections of lower energy. A reaction between such an exciton and an adjacent azide ion can only occur after overcoming an energy barrier. Thus the photolytic reaction should require a small energy of activation. We find that in the present studies, the photolysis requires an energy of activation of 1.40 and 1.75 kcal/mole for samples I and II, respectively.

Diffusion Controlled Photolytic Rate

We assume that

(a) The radiation is absorbed in the bulk of the azide at special positions.

(b) The excitons are produced at all sites where radiation is absorbed subject to the restriction placed by quantum efficiency.

(c) Molecular nitrogen produced by the reaction of trapped exciton with azide ion diffuses towards the surface where it escapes to the atmosphere.

(d) At any time the concentration of molecular nitrogen at the surface is zero.

(e) The rate of production of excitons and therefore the rate of production of molecular nitrogen at the boundary $x = 0$ decreases progressively with increase in time.

$$dn/dt = N_0 Ik \exp(-kt) \tag{11}$$

where k is a rate constant, N_0 is the number of azide ions at special positions at the beginning of the photolysis and I is the intensity.

(f) The boundary at $x = 0$ is set in such a way that the diffusion length is an average and remains constant.

This situation causes a nonstationary problem. The rate of decomposition at the boundary at $x = 0$ depends on the concentration of potential exciton generating sites at the interface. The concentration gradient at $x = 0$ for a linear boundary condition is

$$D\frac{\partial n}{\partial t}\bigg|_{x=0} = kIN_0. \tag{12}$$

The solution of the differential equation (2) with the boundary conditions stated in Eq. (12) and $n(x,0) = 0$ comes out as

$$n = N_0 I\left[\operatorname{erf}\left(\frac{x}{2(Dt)^{1/2}}\right) + \exp\left(\frac{kx}{D} + \frac{k^2 t}{D}\right) \times \operatorname{erfc}\left(\frac{kt^{1/2}}{D^{1/2}} + \frac{x}{2(Dt)^{1/2}}\right)\right]. \tag{13}$$

The diffusion flux at the boundary $x = 1$ which is equal to the macroscopic reaction rate is found by differentiating the above expression.

$$J = kIN_0 \exp\left(\frac{k^2 t}{D}\right) \operatorname{erfc}\left(\frac{kt^{1/2}}{D^{1/2}}\right). \tag{14}$$

For small t,

$$J = kIN_0, \tag{15}$$

and the reaction is limited by kinetic control. This is due to the infinitely large initial concentration gradient and the diffusion rate. Since erfc decreases much faster than exp $(-x^2)$ with an increase in the argument x, we retain the first term for the asymptotic expansion for J at large t. Thus

$$J = IN_0\frac{D^{1/2}}{(\pi t)^{1/2}} = \frac{dn}{dt}\bigg|_{x=1} = \frac{d\alpha}{dt}, \tag{16}$$

or

$$\alpha = \text{Constant}\cdot I(t)^{1/2}.$$

which is the form of expression to which the experimental results could be fitted. Assuming that the domain of kinetic control has an extremely short life we get a diffusion controlled rate almost from the beginning of photolysis. This indeed is the experimental finding.

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