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NICKEL AZIDE PHOTOLYSIS

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Photolysis of anhydrous NiN_6 at 30° under the action of high pressure Hg arc is reported. The sample for photolysis studies is prepared by treating aqueous nickel azide solution with excess of AnalaR dimethyl ketone. The pressure of N developed during photolysis under steady state conditions at constant intensity is a linear function of $t^{1/2}$ and dark rate analysis suggests that the dependence on $t^{1/2}$ should be due to the diffusion of N from reaction site to the surface of solid azide. Absence of photoconduction in the wavelength range of the irradiating radiation suggests that excitons are the reactive species and the linear dependence of the rate of photolysis on intensity is interpreted in terms of the reaction of a trapped exciton with adjacent azide ion.

Stability of azides varies over a very wide range i.e. from most stable azides of s^1 elements to some highly sensitive explosive azides of *d*-block elements. At present no satisfactory theory correlates quantitatively the azide explosive character and the ionic character of the azide metal bond. Apart from the azides belonging to d^9 and d^{10} transitional systems for which the results on decomposition kinetics are reported to a certain extent [1, 2], none of the transitional metal azides have been studied for their decomposition due to their high explosive nature. Photolysis of nickel azide has not been studied in the past since it explodes very violently on gentle rubbing or on applying pressure [3]. Results on photolysis of nickel azide are now presented.

Experimental

Nickel azide was prepared by an adaptation of the method recommended by Kemp [4] for potassium azide. Hydrazoic acid was distilled onto a suspension of nickel carbonate in water. Hydrazoic acid was generated by dropwise addition of 1 : 1 H_2SO_4 to 13% NaN_3 solution at 70–80°.

After nickel carbonate dissolved completely, a slight excess of hydrazoic acid was added to maintain an acidic environment. The solution of nickel azide was filtered and treated with excess of AnalaR dimethyl ketone. A sandy green precipitate thus obtained was analysed volumetrically [5] to be $Ni(N_3)_2$. The sample was always stored over P_2O_5 in a dessicator under vacuum and extreme care was taken during handling because of its hygroscopic nature.

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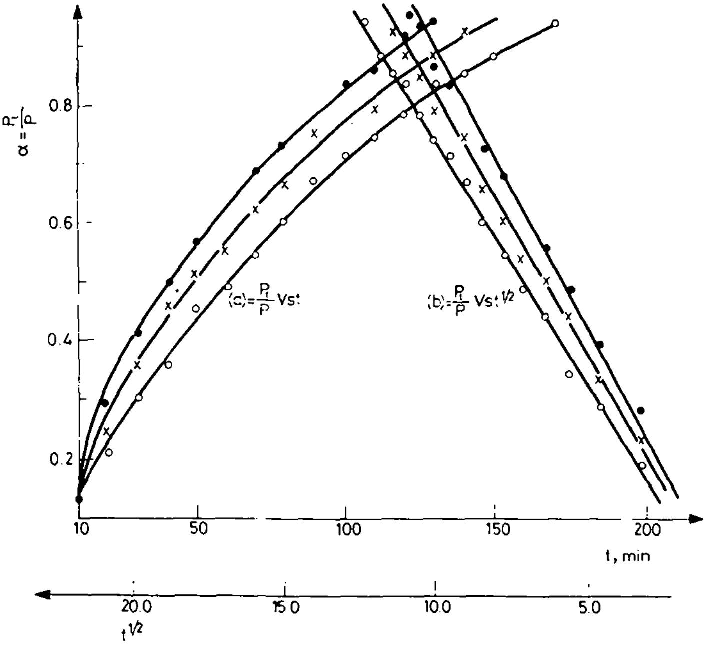

Fig. 1. Decomposition of $Ni(N_3)$ at three different intensities

A conventional vacuum system was used for the photolysis studies on nickel azide. The photolysis cell consisted of a Pyrex glass tube 2.5 cm in diameter and 10 cm in length and having a B-24 quick fit joint at the top end. A 5 mm thick optically plane quartz window of 3.5 cm diameter was sealed on top of the cell by means of piecene wax and irradiation of the sample was done through it. The source of ultra violet light was HPK-125 (80W) Hg lamp which has a strong emission at 2537 Å. In order to obtain the maximum intensity no filters were used and in order to obtain the different intensities the distance of the lamp from the specimen was varied. In a typical photolysis run, the nickel azide sample was spread uniformly at the bottom of the cell and was evacuated for 24 hours at 10^{-6} mm of Hg, before studying photolysis. Photolysis has been carried out at a number of intensities at 30° on well aged $Ni(N_3)_2$ sample and for each photolysis run a fresh $Ni(N_3)_2$ sample was used, but the results on three different intensities are presented in Fig. 1.

Results and discussion

Irradiation of aged fresh sample of $Ni(N_3)_2$ with UV radiation results in spontaneous evolution of nitrogen and the rate of evolution of nitrogen progressively decreases with time. The degree of decomposition α (the ratio of the pressure of

N_2 at any time 't' to the pressure of N_2 in the event of complete decomposition) varies as $t^{1/2}$. The rate equation for photochemical decomposition can be written as

$$\frac{d\alpha}{dt} = a/\alpha$$

Where a is a constant which includes intensity terms. On solving for α we get

$$\alpha = \sqrt{2at} + \text{Constant} \qquad \text{At} \quad t = 0$$

$$\alpha = 0 \quad \therefore \ \text{Constant} = 0$$

or $$\alpha = \sqrt{2at}$$

The dependence of the rate of photolysis on intensity can be determined by plotting $\sqrt{2a}$ versus intensity of irradiation 'I' which is found to be a straight line (Fig. 1)

$$\therefore \ a = \frac{b^2 I^2}{2} \qquad \text{where } b \text{ is a constant}$$

and

$$\frac{d\alpha}{dt} = \frac{bI}{2\sqrt{t}}$$

meaning that the rate of photolysis is linearly dependent upon intensity.

The results on dark reaction (reaction after the UV lamp is switched off) are reported in Fig. 2. The dark reaction in the present investigation was found to be intensity dependent and the dark reaction rate constant was independent of intensity. The dark reaction is therefore likely to be a diffusion of nitrogen molecules from the interior of the solid to the surface and the amount of nitrogen accumulated will be directly proportional to the intensity of irradiation.

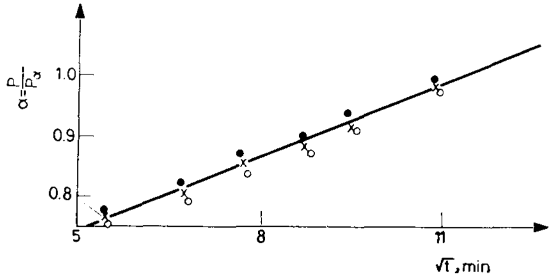

Fig. 2. Dark reaction of $Ni(N_3)_2$ at three different intensities

Upon solving Fick's diffusion equation with an intensity dependent first order boundary conditions, we get

$$\frac{d\alpha}{dt} = \mathrm{No}\, I\sqrt{D/t}$$ (where No = Total azide ions at special sites at the beginning of photolysis)

or

$$\alpha = \text{Constant } xIx\sqrt{t}$$

This is in agreement with the experimental results.

Diffused reflectance spectra and absence of any detectable photoconductivity in the region of irradiation suggests the formation of excitons during the decomposition. Bimolecular decomposition, whereby an exciton trapped at a special site X notably near dislocation where selection rules are relaxed interacts with an adjacent azide ion resulting in chemical reaction with consequent evolution of N_2 [6], will be

$$N_3^- + h\nu \overset{K_1}{\rightleftharpoons} N_3^{-*} \tag{1}$$

$$N_3^{-*} + X \overset{K_2}{\rightleftharpoons} N_3Xe^* \tag{2}$$

$$N_3Xe^* + N_3^- \xrightarrow{K_3} 3N_2 + X + 2(e) \tag{3}$$

$$N_3Xe^* \rightleftharpoons N_3 + X + (e) \tag{4}$$

Under steady state considerations

$$\frac{d}{dt}[N_3^{-*}] = k_1I + k_{-2}[N_3Xe^*] - k_{-1}[N_3^{-*}] - k_2[N_3^{-*}]$$

If we assume that the concentration of excitons is determined mainly by the reaction (1) then:

$$[N_3^{-*}] = k_1I/k - 1 + k_2$$

Similarly under steady state the $[N_3Xe^*]$ will be

$$[N_3Xe^*] = \frac{k_2[N_3^{-*}]X}{k_{-2} + k_3}$$

$$\frac{dN_2}{dt} = k_3[N_3Xe^*][N_3^-]$$

Since the degree of decomposition is small $[N_3^-]$ can be considered to be constant.

$$\frac{dN_2}{dt} = k_3[N_3Xe^*] = \frac{Xk_3k_2k_1I}{(k_{-2} + k_3)(k_{-1} + k_2)}$$

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

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References

1. F. P. BOWDEN and J. MACAUSLAN, Nature, 178 (1967) 408.
2. F. P. BOWDEN, Proc. Roy. Soc. London, Ser A (1959) 146.
3. L. WOHLER and F. MARTIN, J. Chem. Soc., 112 (1917) 383.
4. M. D. KEMP, J. Chem. Educ., 37 (1962) 142.
5. TAYLOR, Cited in Kolthoff and Elving, "Treatise on Analytical Chemistry" Part II, Vol. 5. Interscience Publishers New York.
6. P. W. M. JACOBS, F. C. TOMPKINS and D. A. YOUNG, Discussions Faraday Soc., 28 (1959) 234.