GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 7, NO. 1 JANUARY 2001:73 - 79
COPYRIGHT (C) BACHUDO SCIENCE CO. LTD. PRINTED IN NIGERIA. ISSN 1118-0579

PHOTOLYSIS OF NICKEL HYDROXY AZIDE

I. IKORA IROM

(Received 17 March, 1999; Revision accepted 23 September, 1999)

ABSTRACT

Photolysis of nickel hydroxy azide at 308^{0}K is compared with that of nickel azide under similar considerations. Nickel azide sample was prepared by adapting the method of Brauer while nickel hydroxy azide was obtained by dehydrating the dihydrate of nickel azide crystals, ($Ni(N_3)_2.2H_2O$) and exposing to atmospheric moisture. The rate of evolution of nitrogen at constant temperature and different intensities, decreases with time. The pressure of nitrogen produced with time varies directly as at all intensities. The rate of photolysis at constant temperature at intervals of time varies with intensity. Absence of photoconduction in the region reveals that excitons are the main reactants which get trapped in adjacent azide ions. This is evident in the linear dependence of the rate of photolysis on the intensity. The rate of photolysis of $Ni(OH)N_3$ is observed to be lower than that of $Ni(N_3)_2$ by about a factor of 10.

Keywords:

Photolysis, Azide, Quantum Yield, Lattice imperfection, Holes.

INTRODUCTION

Azides are very important explosives, detonators, for oil exploration, catalysts, synthetic raw materials and as a source for generating pure metals. Azides such as AgN_3, $Pb(N_3)_2$, $Hg(N_3)_2$, tri-azidotrinitro -benzene, are primary explosives and are, therefore, used to initiate detonation of the less sensitive explosives.

Studies have recently been conducted on the use of azidenucleosides, namely AZT (3^1-azido-3^1 dioxythyimidine) and CS-85 for the treatment of acquired immune deficiency syndrome, (AIDs), and aids-related complex, (Robins, 1986).

Azido organic compounds are more common in the literature than their inorganic counterparts. This is because of the difficulty of preparing and handling inorganic complex azides and also due to their explosive sensitivity. Decomposition reactions of some inorganic azides such as alkali metals, Ti(I) and Cu(I) have, however, been presented (Foster et al, 1976, Edgar, 1976, Winkler, et.al. 1975 and Zakhoarov et al, 1975). Decomposition usually occurs when the azide is subjected to heat, light, ionising radiation (Fox et.al. 1977, Garret et.al, 1977), impact and friction, (Avrami and Haberman, 1977).

Heavy metal azides generally undergo decomposition with the evolution of large amounts of heat which, in most cases, cause explosion and even [illegible]. This behaviour has greatly impaired [illegible] studies of heavy metal azides. Ekop has synthesized and characterized the azide complexes of Ni(II) (Ekop, 1989). He reported that the decomposition curves for photolysis, photodecomposition and thermal decomposition for the complexes, $[Ni(NH_3)_6](N_3)_2$, $[Ni(NH_3)_5\,N_3]\,N_3$ and $[Ni\,(NH_3)_4\,(N_3)_2\,(N_3)_2]$ are similar. Ekpe, (1988) and Akwaowo, (1989) have respectively reported similar observations for $Co(N_3)_2$ and $Fe(N_3)_2$. The present investigation aims at determining the effect of the presence of hydroxy group on the photostability of nickel azide.

Nickel azides are technologically useful especially in the fields of medicine and mining. Their high sensitivity to shock, friction, and impact, however, limits the scope of application. Investigation on the photolysis of $Ni(OH)N_3$ is an effort to find a milder form of the azide which could invariably be safer to handle.

EXPERIMENTALS

One sample each of normal nickel azide, ($Ni(N_3)_2$ and nickel hydroxy azide $Ni(OH)N_3$, was prepared using the following scheme: Nickel azide was prepared using [illegible] the preparation of barium azide (Brauer, 1963). The hydrated nickel azide crystals were dehydrated over P_2O_5 and part of the anhydrous crystals were stored over P_2O_5 for 45 days before photolysis studies were conducted on the sample (referred to as Nickel Azide). The remaining part of the anhydrous nickel azide was exposed to moist atmosphere (relative humidity > 80%) for several days and then ground to powder (particles size between -200 to 250 mesh). The sample was again stored over P_2O_5 for 45 days before investigation. This sample was referred to as nickel hydroxy azide sample.

Photolysis studies of the two samples were carried out in a photolysis decomposition assembly (fig.1). The photolysis cell consisted of a pyrex glass tube 2,0cm in diameter and 12cm in length having a quickfit joint at the end. A 3mm thick optically plane quartz window was sealed onto the top of the cell by means of pycene wax and irradiation of the sample was done through the window. The cell was connected to

I. IKORA IROMA Department of Pure and Applied Chemistry, University of Calabar, Calabar, Nigeria

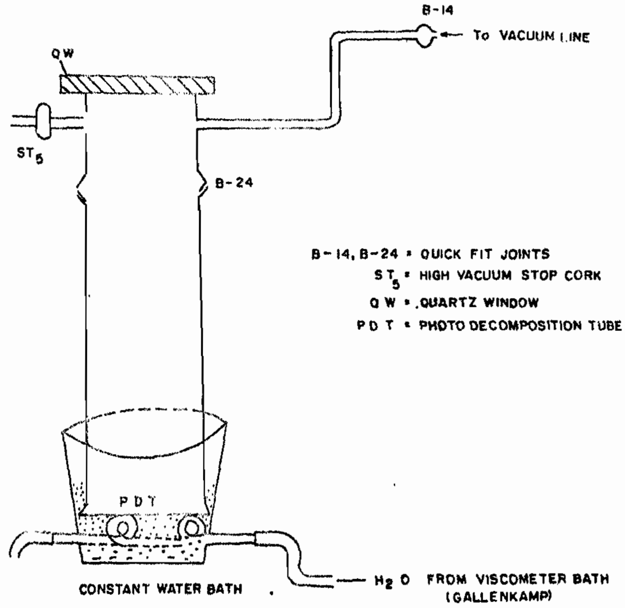


Fig. 1 - DECOMPOSITION CELL

the vaccum line through a standard joint and a tap. The pressure produced during decomposition was measured with a Mcleod Guage capable of measuring pressure up to 10^{-6}torr (100μm Hg). The total volume of the system (Mcleod Guage + standard volume flask + photolysis cell) was 2.45 litres.

Photolysis of the samples was performed at different intensities (obtained by varying the distance of UV lamp over the photodecomposition cell while the temperature was kept constant by means of a constant temperature water bath jacket which surrounded the cell uniformly. In a particular run of photolysis 50mg of each of the samples was spread uniformly at the bottom of the photolysis cell. After prolonged evacuation, the initial dark rate was measured. Thereafter the accumulated gas was pumped out. The system was again evacuated continuously for 2hrs. The light source was then switched on and the radiation allowed to fall directly on sample in the cell. The pressure of nitrogen accumulated over the sample during the radiation was measured with the Guage as a function of time.

After prolonged photolysis the UV Lamp was switched off and the dark rate of the reaction was studied till it became very nearly equal to the initial dark rate. The initial dark rate was subtracted from the rate of photolysis to obtain the actual photolysis rate.

RESULTS AND DISCUSSION

Irradiation of the two azide samples with full output from a high pressure mercury lamp results in spontaneous evolution of nitrogen. The samples were also subjected to prolonged photolysis for about 1,500mins at constant intensity and temperature. (figs. 6 and 7). The photolysis plots are presented in figs 3a and 2b for both azides.

The decomposition of the two azides vary as $t^{1/2}$ (figs 2b and 3b). The data fitted into a rate equation of the form.

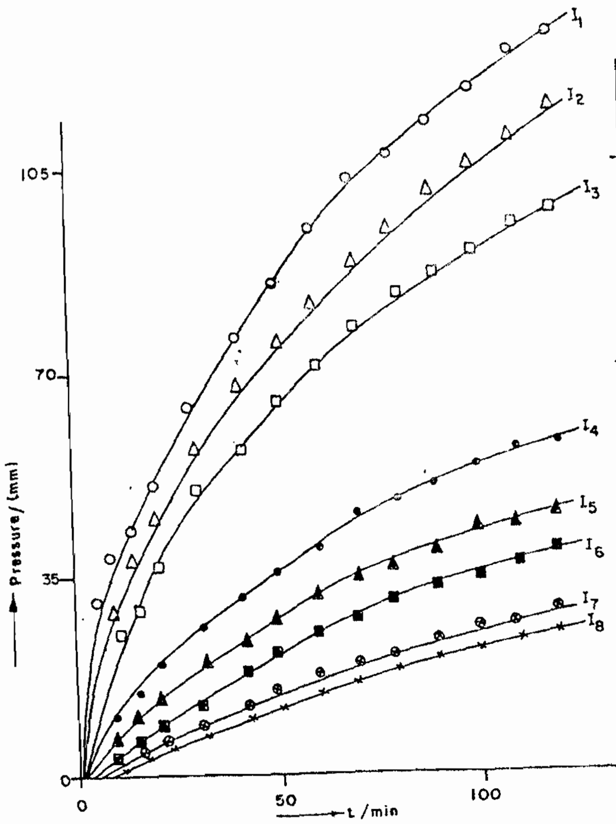


Fig. 2a PHOTOLYSIS OF NICKEL AZIDE AT DIFFERENT INTENSITIES AND 298 K

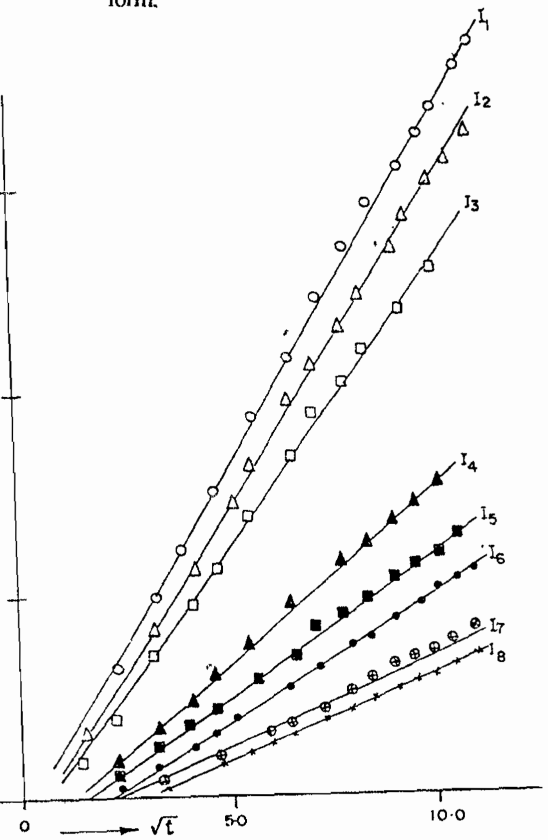


Fig. 2b PLOT OF P vs $\sqrt{t}$ FOR FIGURE 2

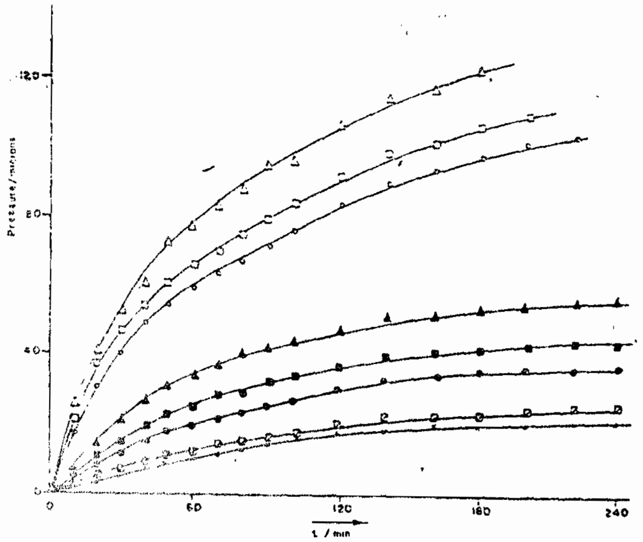


Fig. 3a PLOT OF P Vs t FOR PHOTOLYSIS OF NICKEL HYDROXY AZIDE AT DIFFERENT INTENSITIES AND CONSTANT TEMPERATURE, 308 K

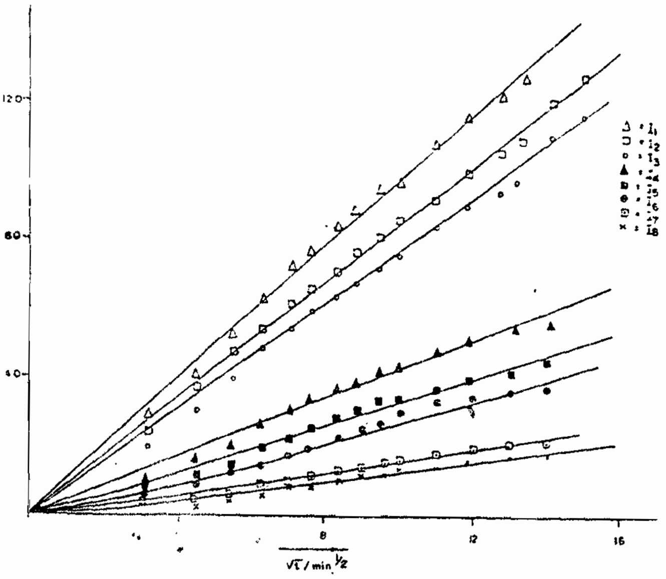


Fig. 3b PLOT OF PRESURE Vs √t FOR Ni(OH) N_3 AT DIFFERENT INTENSITIES AT 308 K

$$P = S.\sqrt{t} \qquad \text{.....(1)}$$

is a constant containing the intensity term.

We can also write,

$$dp/dt = a/p \qquad \text{.....(2)}$$

is a constant containing the intensity term

For p = o at t = o

$$P = \sqrt{2at} = S.\sqrt{t}$$

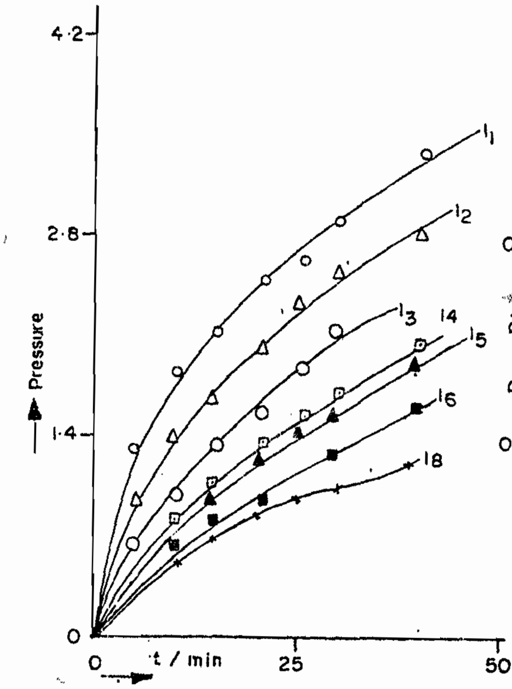
$$\text{where } S = \sqrt{2a}$$

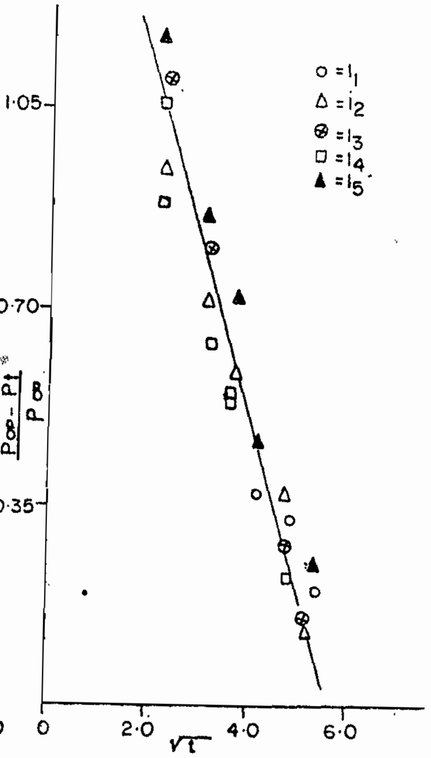
An account of dependence of photolysis rate of both azides on the fractional power of time can be understood from the observations made for the photolysis of barium azide (Thomas, Tompkins, (1951) and Jacobs et al, (1962). They have reported that a decrease in the rate of photolysis of barium azide is independent of the pressure of nitrogen developed over the sample and the nature of the irradiating source. This implies the absence of the effect of molecular nitrogen on the solid matrix. Thus, irrespective of what pressure of nitrogen that prevails over the sample and also the nature of irradiation source (so long as the spectral distribution of intensities is not altered) a sample of a metal azide should photolyse according to the general observations of Jacobs. Tompkins and Young (1959).

The decreasing rate at constant intensity could be explained only if the 'dark reaction' rate is clearly understood. Jacobs, Shaphard and Tompkins (1963) have found that the amount of gas evolved in the dark reaction depends upon both the intensity of light and the duration of irradiation. Any dark reaction observed is the result of the 'light reaction' that has already taken place and the evolution of nitrogen during the dark reaction is simply the liberation or escape of nitrogen that accumulated within the azide lattice and at the reaction interface. Yoganarasimhan and Tompkins (1967) summarized that the rate is. therefore, likely to be due to the diffusion of nitrogen molecules from the interior of the solid to the surface. The accumulation of the gas in the interior. its amount depending upon the irradiating radiation results in a pressure gradient between the reaction interface and the surface. Under such conditions. therefore. the diffusion of nitrogen shows up as intensity dependent dark rate.

If the dark reaction pressures are normalized [ie $(P_\infty-P)/P_\infty$] and plotted against $t^{½}$ the dark-reaction rate constant will be seen to be independent of intensity (ie the plots give straight lines with identical slopes for all intensities, (figs. 4b and 5b). These observations were made for barium azide and also for the nickel azide and nickel hydroxy azide under the present investigation. The fall in the observed rate of photolysis may probably be due to the inhibition of the evolution of nitrogen at the surface which is due to a slow diffusion in the bulk. The dark reaction of $Ni(OH)N_3$, like $Ni(N_3)_2$, was intensity dependent (figs 4a and 5a). Their dark reaction rate constants were found to be intensity independent (figs. 4b and 5b). The dark reaction pattern imply the diffusion of nitrogen from the bulk of the azide to the surface. The amount of the nitrogen accumulated in the interior depends on the intensity of radiation. Thus the dark reaction rate shows up as intensity dependent. Similar expression has been reported for the diffusion controlled mechanism of photolysis of zinc and cobalt azides (Sood et al, 1988).

The light source used for photolysis was a high pressure mercury lamp with strong emission at 365.5, 313.0 and 253.7nm among other weaker lines (Table 1). The diffused reflectance spectra of the two azides recorded on a Unicam SP 700 spectrophometer in the UV and visible regions show absorption maxima in the range, 210-270nm (for $Ni(N_3)_2$) and 210-260nm (for $Ni(OH)N_3$). (Irom, 1990). Sood and Nya (1981) have reported that $Ni(N_3)_2$) did not show appreciable photoconduction when it absorbs radiation in this region. This implies that the absorption of radiation in this region results in excitation of an electron from the valence band of the anion to an exciton level. Similar





4a PHOTODECOMPOSITION OF NICKEL AZIDE DARK REACTION Fig. 4b

observations have been made in the case of alkali metal azides (Deb, 1963, 1961). According to Jacobs, Tompkins and Young (1959) the excitons so produced can be mobile within the lattice and could either get:

(i) Deactivated by interaction with phonons accompanied by a reversion of the electron to the valence band or,

(ii) Interact with an imperfection (during its characteristic lifetime of 10^{-8} sec) in the crystal resulting in their being trapped and sharing electrons in the process with the imperfections or special sites. The trapped excitons may dissociate to mobile holes and electrons which ultimately recombine at traps. However, if favourably disposed, the trapped exciton can interact with an adjacent azide ion resulting in chemical reaction evolving nitrogen.

The rate of photolysis of nickel azide has already been found to be proportional to the number of special sites, 'S' (traps) and the intensity, I, of radiation (Sood and Nay, 1981). Our experimental results in figs 2a and 3a show the rate of photolysis of nickel hydroxy azide to be similar to that of nickel azide. The decrease in the rate of photolysis can be explained in terms of the destruction of traps as the photolysis progress. This decrease consequently results in lowering the photolysis rate. The decrease in the rate of photolysis is expected to be small compared to the observed value of the rate due to the inhibited diffusion of molecul nitrogen. The former will be prominent during the initi stages of photolysis while the latter is the dominai factor during the later stages. The observation in th present investigation is that the rate of photolysis c nickel hydroxy azide with unfiltered UV light is muc lower than that of nickel azide. A possible explanatic has been offered (Irom, 1990) as follows:

(i) The presence of photolytically inert OH ion in $Ni(OH)N_3$ and,

TABLE 1

SPECTRA DISTRIBUTION TERMS OF DIFFERENT WAVELENGTHS COMPRISING THE EMISSION SPECTRUM OF THE SOURCE OF LIGHT (HPK 125W PHILIPS)

WAVELENGTH(nm)	PERCENTAGE INTENSITY (%)
248.2	1.70
253.7	8.50
265.3	3.74
269.9	0.68
280.4	1.70
289.4	1.02
296.7	3.06
302.5	4.76
313.5	10.54
334.1	1.36
365.5	17.34
404.7	6.12
435.8	11.90
491.6	0.68
546.1	14.96
598.0	11.90

The values are based on electrical and ordinary data of the lamp supplied by the company

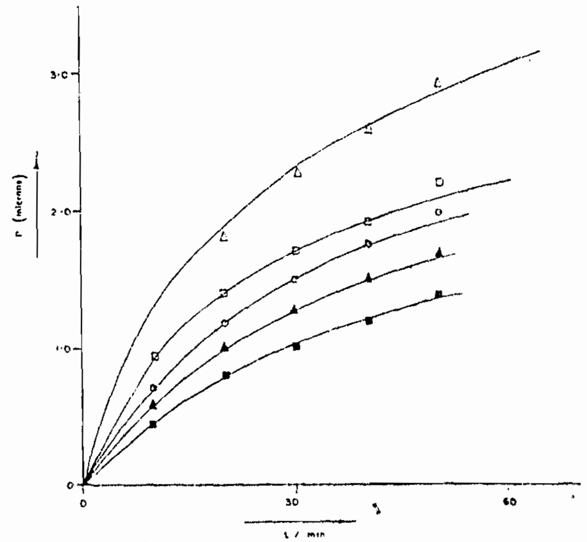


Fig. 5a PLOT OF P Vs t DARK REACTION OF Ni (OH) N

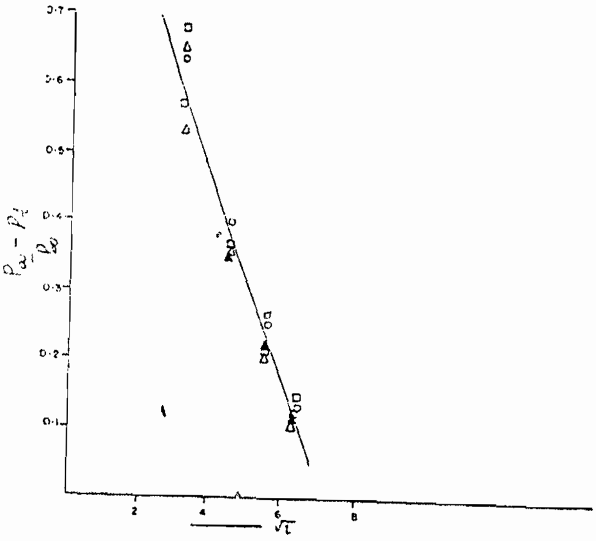


Fig. 5b PLOT OF $(P_\alpha - P_t)/P_\alpha$ Vs $\sqrt{t}$ FOR DARK REACTION OF Ni (OH) N_3

(ii) Smaller length of the maximum absorption edge (210-260nm) as compared to that of 210-270nm for $Ni(N_3)_2$ shown in the diffuse reflectance spectra of the azides.

QUANTUM YIELD

The UV region of the emission spectra of the high pressure mercury lamp used for photolysis of nickel azide consists of 248 < λ <365.5nm. From the diffused reflectance spectra of the azide, it is obvious that, although the wavelengths in the region 280-330nm could be photolytically active, photodecomposition of nickel azide is brought about mainly by 240nm< λ <280nm. Since isolation of wavelengths in this region could not be achieved the calculated quantum yield will be an average of wavelengths in the region.

Since the reflectivity of the surface of the sample is extremely difficult to measure it is not easy to estimate the fraction of the incident light energy actually absorbed by the sample. However, by analogy with Jacobs and Tompkin's (1952) observation on KN_3, it has been assumed that 20% of the incident radiation is lost by reflection and scattering. Moreover, the average intensity of wavelengths in the region 248nm< λ <280nm calculated from the spectral distribution of the light source is about 17% of the total. After considering these factors, the value of the intensity of light actually absorbed by the sample was obtained as

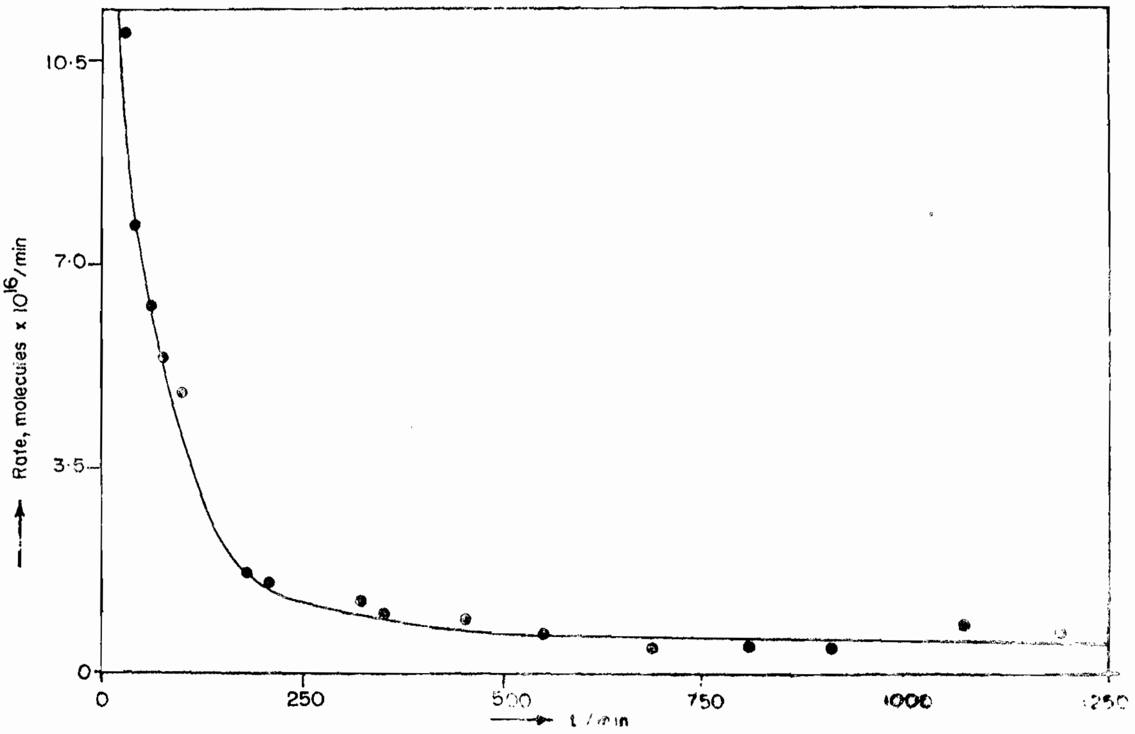


Fig. 6 PROLONGED PHOTOLYSIS OF NICKEL AZIDE-RATE VS TIME

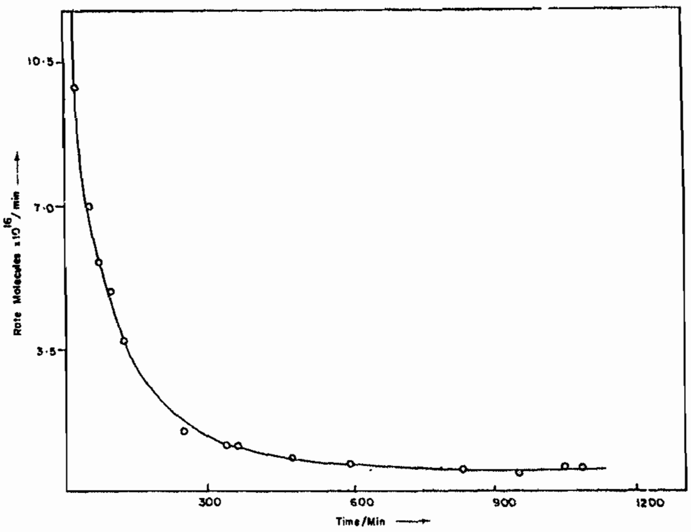


Fig 7 PROLONGED PHOTOLYSIS OF NICKEL HYDROXY AZIDE RATE Vs TIME

1.95 x 10^{15} quanta sic cm-^{2}. Since the rate of photolysis of nickel azide continuously decreases with time, the quantum yield will also decrease in that order. The rate measured after 10 minutes of start of the reaction was 10.87 x 10^{16} molecules min^{-1} and 0.49 x 10^{16} after 1200 min (fig. 6). The area of the exposed surface of the sample was 3.14cm-^{2}. Thus the rate of photolysis, in molecules cm^{-2} sec^{-1} was 5.8 x 10^{14} after 10 minutes and 0.3 x 10^{14} after 1200 minutes. Since the number of molecules of $Ni(N_3)_2$ decomposed will be one third of the number of molecules evolved. $\frac{1}{3}[Ni(N_3)_2 \rightarrow \frac{1}{3}Ni + N_2]$. the number of molecules decomposed per second per square cm-^{2} in the two cases are 1.93 x 10^{14} and 0.1 x 10^{14} respectively. The quantum yield is given by

$$Q = \frac{\text{number of molecules decomposed}}{\text{number of quanta absorbed}}$$

Thus the quantum yield is calculated to be 2 x 10^{-2}. Making similar assumptions as in the case of nickel azide, the quantum yield of photolysis of nickel hydroxy azide was calculated from the results of prolonged photolysis of the compound (fig. 7). The quantum yield after 10 minutes of start of reaction was about 1.8 x 10^{-1}. The continuously decreasing quantum efficiency reached a steady state value of 6.5 x 10^{-3} after about 800 minutes of photolysis. Thus, the final quantum efficiency of a $Ni(OH)N_3$ of 6 x 10^{-3} compared to that of $Ni(N_3)_2$ of 2 x 10^{-2} is lower by an order of 10. Thus, photolysis of $Ni(OH)N_3$ is about 10 times lower than that of $N(iN_3)_2$. Nickel hydroxy azi de could, therefore, be safer to handle in all applications in which the nickel azides are required.

REFERENCES

Akwaowo, B. P., 1989. Photo and thermal decomposition of iron azides; M.Sc. Thesis, University of Calabar, Calabar, Nigeria, (unpubl.).

Avrami, L. and Haberman, J., 1977. Sensitivity of explosive azides to heat and nuclear reaction. In: Energetic materials; (Fair, H. D. and Walker, R. F.) (Editors), Plenum, New York, Vol. 2 (Eng), pp. 199-247.

Brauer, 1963. Handbook of preparative inorganic chemistry; Acard. Press, NewYork, 1: 942pp.

Deb, S. K., 1963. Spectra of metallic azide thin films; Trans. Faraday Soc. 1423.

Deb, S. K., 1963. Photoconductivity in potassium azide; J. Chem. Phys. 35: 2122.

Edgar, F. Jr., 1976. Thermolysis of alkali and related azides; J. Chem. Thermodyn.8(8), 656-573.

Ekop, A. S. 1989. Thermal and photodecomposition of nickel azide complexes Ph.D thesis, University of Calabar, Nigeria (unpubl.).

Ekpe, E. E., 1988. Characterization and decomposition of Cobalt azides; Ph.D.Thesis, University of Calabar, Nigeria.

Foster, D. L. Wagner, K. A. and Laskar, A. L., 1976. Growth and characterization of potassium and rubidium single crystal; J. Cryst. Growth. 32(1), 33-6.

Fox, P. G. and Hutchinson, R. W., 1977. Slow thermal decomposition of inorganic azides. In : Energetic materials. Fair, H. D. and Walker, R. F. (Editors), Plenum, New York, Vol. 1 (Eng), pp. 251-284.

Garret, w. L., Marinkus, P. L. Owen, F. J. and Wiegand, D.A., 1977. Imperfection and radiation induced decomposition of azides, in Energetic materials, Fair, H. D. and Walker, R. F.(Editors), Plenum, New York, Vol. 1 (End) pp.285-382.

Irom, I. I., 1998. Photodecomposition studies of nicke azides Ph.D Thesis, University of Calabar Nigeria, (unpubl).

Jacobs, P. W. M.; Tompkins, F. C. and PaiVencker,R., 1962 Photodecomposition of $Ba(N_3)_2$; J. Phys. Chem. 66,1113.

Jacobs, P. W. M. Tompkins, F. C. and Young,D.A.(1959) Photodecomposition of alkali azides; Dis Faraday Soc., 28: 234.

Jacobs, P. W. M. Shaphard, J. G. and Tompkins, F. C. 1963. In reactivity of solids: G. M. Shawb (Editors), Ellsevier Amsterdam, p. 509.

Jacobs, P. W. M.; Tompkins, F. C. and Pai Verneker, R., 1962. Photodecomposition of arium azide; J. Phys. Chem.

Robins, R. K., 1986. Synthetic antiviral agents; Chem. and Eng. News; (Jan. 27), 28-40.

Sood, R. K. and Nya, A. E., 1981. Photolysis of Ni(N_3)$_2$. J. Therm. Anal. 21: 379-383.

Sood, R. K., Zolt, L. and Ekop, A. S., 1988. Diffusion contolled photolytic rates: J. Trop. Sc. Vol. 1 (1). 14o-50.

Thomas, J. G. N. and Tompkins, F. C., 1951. Photo decomposition of Ba(N_3)$_2$; Proc. Roy. Soc., A209. 550; A210, 111.

Winkler, T. Herwing, G.; Spath, H. T. Hagen, T., Tork K. and Karl, 1975. Phase diagrams of the ceasium azide zinc azide and potassium azide systems; Monastch Chem. 10(10): 533-545.

Yoganarasim han S. R. and Tompkins. F. C., 1967. Decompositionof Ba(N_3)$_2$; Reports submitted t Imperial College, London. 123.

Zakharov, Yu. A.; Shechkov, G. T. and Baklykov, S. P., 1975. Experimental Study on the Mechanism of slow Thermal Decomposition Turning into explosion; Tomsk Politekh Inst., 6: 80-84.