PHOTOLYSIS OF NICKEL HYDROXY AZIDE

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ABSTRACT

Photolysis of nickel hydroxy azide at 308 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(N₃)₂.2H₂O) 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 varied directly as at all intensities. The rate of photolysis at constant temperature at intervals of time varies with intensity. Absence of photoconductivity in the region reveals that excites 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)N₃ is observed to be lower than that of Ni(N₃)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 Ag₃N, Pb(N₃)₂, Hg(N₃)₂, tri-azidatrimeto-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 azidone derivatives, namely AZT (3'-azido-3'-dideoxythymidine) and CS-65 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 been presented (Foster et al, 1976, Edgar, 1976, Winkler, et al. 1975 and Zakharov et al. 1975). Decomposition usually occurs when the azide is subjected to heat, light, ionizing radiation (Fox et al. 1977, Garret et al. 1977), impact and friction, (Avnani and Haberma, 1977).

Heavy metal azides generally undergo decomposition with the evolution of large amounts of heat which, in most cases, cause explosion and even fire. This behaviour has greatly impaired the 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(NH₃)₄]²⁺,[Ni(N₃)₂], [Ni(NH₃)₂(N₃)₂] and [Ni(NH₃)(N₃)₂(N₃)] are similar, Eke, (1988) and Akwaowo, (1989) have respectively reported similar observations for Cu(N₃)₂ and Fe(N₃)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)N₃ 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(N₃)₂) and nickel hydroxy azide Ni(OH)N₃, was prepared using the following scheme: Nickel azide was prepared using aqueous potassium azide (Brauer, 1963). The dihydrated nickel azide crystals were dehydrated over P₂O₅ and part of the anhydrous crystals were stored over P₂O₅ 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 280 to 250 mesh). The sample was again stored over P₂O₅ 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 2,6 cm in diameter and 12 cm 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 pyrolytic wax and irradiation of the sample was done through the window. The cell was connected to...
the vacuum line through a standard joint and a tap. The pressure produced during decomposition was measured with a McLeod Gauge capable of measuring pressure up to $10^{-4}$torr (100μm Hg). The total volume of the system (McLeod Gauge + 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 $t^2$ (figs. 2b and 3b). The data fitted into a rate equation of the form.
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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 to \(P/P_0\) and plotted against \(t\), the dark–reaction rate constant will be seen to be independent of intensity (i.e., the plots give straight lines with identical slopes for all intensities, (figs. 4a and 5a). These observations were made for barium azide and also for the nickel azide and nickel hydroxy azide under the present investigation. The full 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 \(\text{Ni(OH)}_2\), like \(\text{Li(N})_2\), 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 implies 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 irradiation. 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 253.7 nm among other weaker lines (Table 1). The diffused reflectance spectra of the two azides recorded on a Unicam SP 700 spectrophotometer in the UV and visible regions show absorption maxima in the range 210-270 nm for \(\text{Ni(N}2\text{)}_2\) and 210-260 nm for \(\text{Ni(OH)}_2\). (from, 1990). Sood and Nya (1981) have reported that \(\text{Ni(N}2\text{)}_2\) 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 azide to an exciton level. Similar
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 $10^{10}$ 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 excition 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 process. 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 molecular nitrogen. The former will be prominent during the initial stages of photolysis while the latter is the dominant factor during the later stages. The observation in the present investigation is that the rate of photolysis of nickel hydroxy azide with unfiltered UV light is much lower than that of nickel azide. A possible explanation has been offered (Irom, 1990) as follows:

(i) The presence of photolytically inert OH ions in Ni(OH)N₂ and,

<p>| TABLE 1 |
| SPECTRA DISTRIBUTION TERMS OF DIFFERENT WAVELENGTHS COMPRISING THE EMISSION SPECTRUM OF THE SOURCE OF LIGHT (HPK 125W PHILIPS) |</p>
<table>
<thead>
<tr>
<th>WAVELENGTH (nm)</th>
<th>PERCENTAGE INTENSITY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>248.2</td>
<td>1.70</td>
</tr>
<tr>
<td>253.7</td>
<td>8.50</td>
</tr>
<tr>
<td>265.8</td>
<td>3.74</td>
</tr>
<tr>
<td>269.9</td>
<td>0.68</td>
</tr>
<tr>
<td>280.4</td>
<td>1.70</td>
</tr>
<tr>
<td>289.4</td>
<td>1.02</td>
</tr>
<tr>
<td>296.7</td>
<td>3.66</td>
</tr>
<tr>
<td>302.5</td>
<td>4.76</td>
</tr>
<tr>
<td>313.5</td>
<td>10.54</td>
</tr>
<tr>
<td>334.1</td>
<td>1.36</td>
</tr>
<tr>
<td>365.4</td>
<td>17.34</td>
</tr>
<tr>
<td>404.7</td>
<td>6.12</td>
</tr>
<tr>
<td>415.8</td>
<td>11.90</td>
</tr>
<tr>
<td>491.6</td>
<td>0.68</td>
</tr>
<tr>
<td>546.1</td>
<td>14.36</td>
</tr>
<tr>
<td>598.0</td>
<td>11.90</td>
</tr>
</tbody>
</table>

The values are based on electrical and optical data of the lamp supplied by the company.
(ii) Smaller length of the maximum absorption edge (210-260nm) as compared to that of 210-270nm for \( \text{Ni(N}_3\text{)}_2 \), 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 < \( \lambda \) < 350 nm. From the diffused reflectance spectra of the azide, it is obvious that, although the wavelengths in the region 280-330 nm could be photolytically active, photodecomposition of nickel azide is brought about mainly by 240 nm < \( \lambda \) < 280 nm. 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 \( \text{KN}_3 \), 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 < \( \lambda \) < 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...
1.95 x 10^{14} \text{ quanta} \text{ cm}^{-2}. \text{ 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^{12} \text{ molecules min}^{-1} \text{ and} 0.49 \times 10^{12} \text{ after 1200 min (fig. 6). The area of the exposed surface of the sample was} 3.14 \text{ cm}^{-2}. \text{ Thus the rate of photolysis, in molecules cm}^{-2} \text{ sec}^{-1} \text{ was } 5.8 \times 10^{14} \text{ after 10 minutes and } 0.3 \times 10^{14} \text{ after 1200 minutes. Since the number of molecules of Ni(N_3)_2 \text{ decomposed will be one third of the number of molecules evolved, } \frac{1}{3} [\text{Ni(N}_3\text{)}_2 \rightarrow \frac{1}{3} \text{Ni} + \text{N}_2 ], \text{ the number of molecules decomposed per second per square cm}^{-2} \text{ in the two cases are } 1.93 \times 10^{14} \text{ and } 0.1 \times 10^{14} \text{ 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 \(2 \times 10^{-2}\). 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 \(1.8 \times 10^{14}\). The continuously decreasing quantum efficiency reached a steady state value of \(0.5 \times 10^{3}\) after about 800 minutes of photolysis. Thus, the final quantum efficiency of a Ni(OH)N\(_3\), of \(6 \times 10^{-3}\) compared to that of Ni(N\(_3\))\(_2\), of \(2 \times 10^{-3}\) is lower by an order of 10. Thus, photolysis of Ni(OH)N\(_3\), is about 10 times lower than that of Ni(N\(_3\))\(_2\). Nickel hydroxy azide could, therefore, be safer to handle in all applications in which the nickel azides are required.

REFERENCES


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