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PHOTOCHEMICAL STUDY OF NICKEL HYDROXY AZIDE THROUGH BENZENE FILTER

I. I. IROM

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ABSTRACT

This paper reports the investigated wavelength region of UV lamp that is actually responsible actually for photodecomposition of the azide and the effect it has on the mechanism of the reaction. The diffuse reflectance spectrum of nickel hydroxy azide shows the azide to absorb radiation at a wavelength range of 210 to 270nm. A benzene filter (which absorbs radiation in the region λ<280nm) is employed as light filter. The filter cuts off the most actinic wavelengths of the light source leaving only a small amount of intensity of radiation to reach the sample without any significant penetration. The result is that the reaction becomes predominantly a surface reaction with a rate which accelerates only when all the available deep surface traps are filled, unlike the case of decomposition using unfiltered radiation.

KEYWORDS: FILTER, ACTINOMETRY TRAPS, EXCITONS.

INTRODUCTION

The effect of the interaction of electromagnetic radiation with matter has been immensely harnessed in many fields of science and technology. The scope of this application is based on three main factors, namely;

(i) The absorption spectrum of the system,
(ii) The transparency of the reaction cell
(iii) The emission spectrum of the radiating source

Mercury lamps of varying pressure are most frequently employed for photo reactions. However they vary in their ability to produce light at different wavelengths. In order to study the effectiveness of light source over different wavelengths some devices are usually employed to isolate desired wavelengths range of the spectrum of the radiating source. They include monochromators, filters and prisms. While filters have the advantages of cheapness, simplicity in operation and production of high intensity, the monochromators rank best in the ability to isolate a narrow range of wavelengths.

Our interest in the present work is to investigate the effectiveness of various actinic wavelengths in the spectrum of the light source that are responsible for the photodecomposition of nickel hydroxy azide.

EXPERIMENTAL

The sample of $Ni(OH)N_3$ used for photodecomposition through filter was obtained as described by Irom, (1990). The sample, labelled NHA3, was aged for at least 10 months before use. Benzene Filter was used to isolate the desired wavelengths.

TABLE 1

ACTINOMETRY OF SOURCE OF LIGHT

Intensity	I_1	I_2	I_3	I_4	I_5	I_6	I_7	I_8
Quanta/sec/15cm^2 x10^{15}	18.1	16.3	14.4	8.1	5.8	4.3	3.0	2.4

TABLE 2

UNFILTERED AND FILTERED PHOTOLYSIS OF SAMPLE AT 298 K AND I_3

Time (mins)	Pressure (microns)	
	Unfiltered	Benzene filter
10	7.04	0.44
20	14.00	0.88
30	18.80	1.00
40	22.80	1.42
50	26.03	1.76
60	28.90	2.20
70	32.00	2.54
80	34.00	2.64
90	36.36	3.08
100	38.12	3.52
110	39.50	4.00
120	41.00	4.10
130	41.75	4.50
140	42.50	4.60

I. I. IROM, Department of Pure and Applied Chemistry, P.M.B. 1115. University of Calabar, Calabar. Nigeria

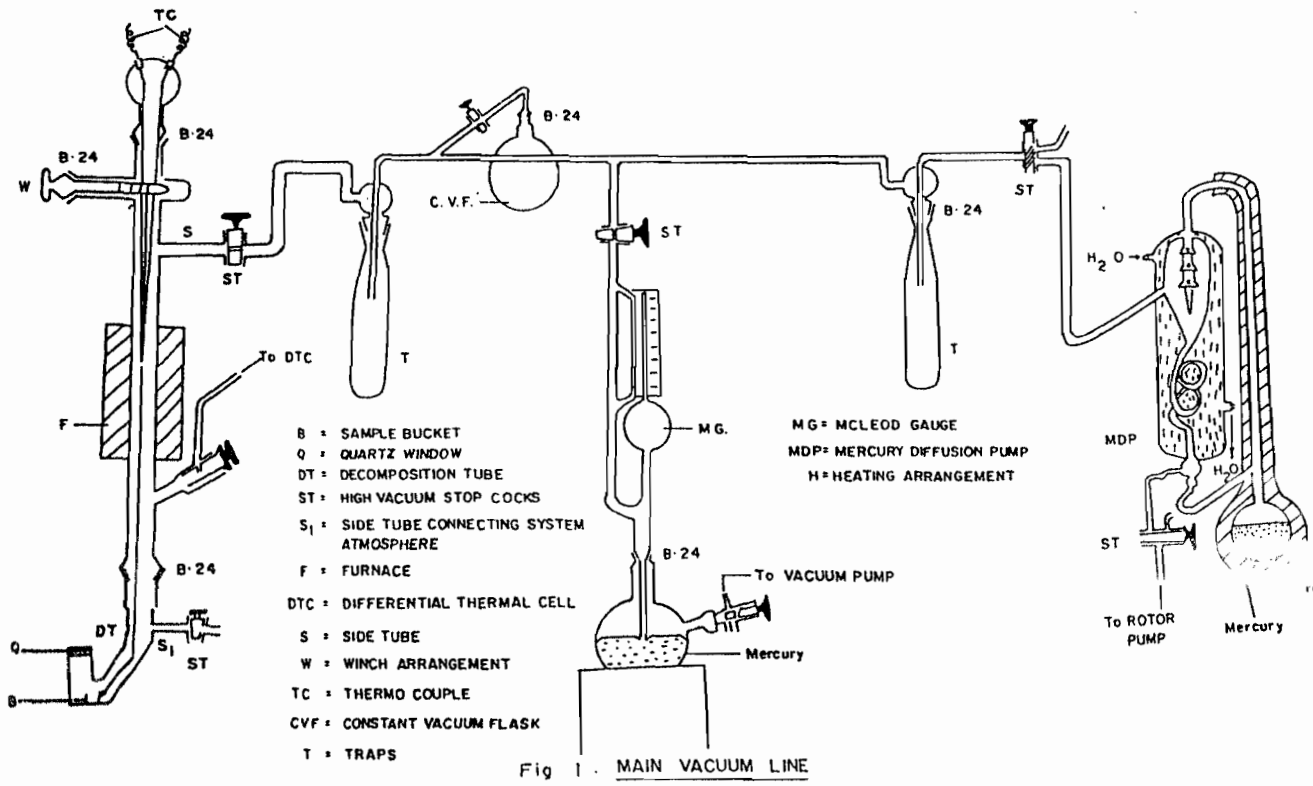

Fig 1. MAIN VACUUM LINE

Pure benzene (free from thiophene) filled in a quartz cell completely absorbs in the region, $\lambda < 280$nm and is transparent to region $\lambda > 289$nm with a maximum ransmission of about 50%. The percentage transmission decreases with time of exposure of the filter to the source of light. The absorption profile of the filter taken after several exposures for different lengths of time is given in ***figure 2.***

Suitable ultraviolet cut-off filters were not available for this work. A circular quartz cell of diameter 2.2cm (to suit the size of the photolysis cell window) with path length of 1cm, filled with thiophene-free benzene was improvised as the required filter. As was reported for the photolysis of the azide using full out put of UV light (Irom, 1990). 50 mg of the sample is spread uniformly in the photolysis cell connected to the main

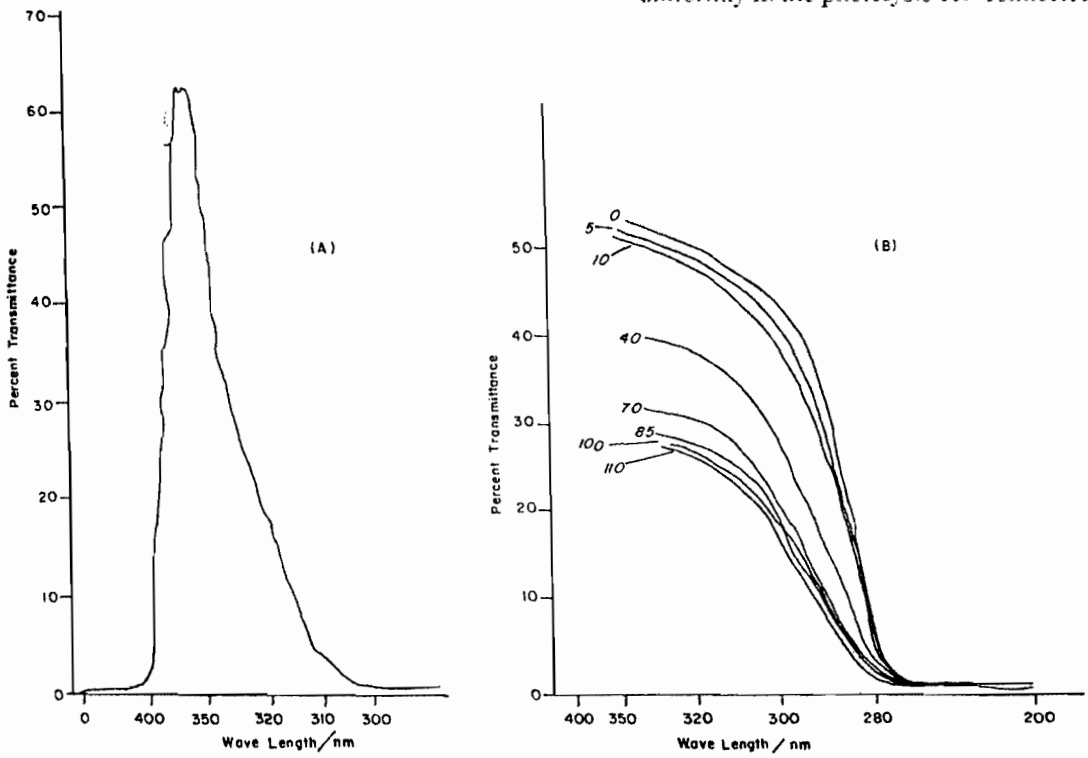

Fig.2 ABSORPTION PROFILE OF (a) FILTER H556 AND (b) BENZENE FILTER-DECREASE IN TRANSMITTANCE WITH TIME OF EXPOSURE OF BENZENE FILTER IS SHOWN. THE TIME (minutes) IS INDICATED WITH ABSORPTION PROFILE

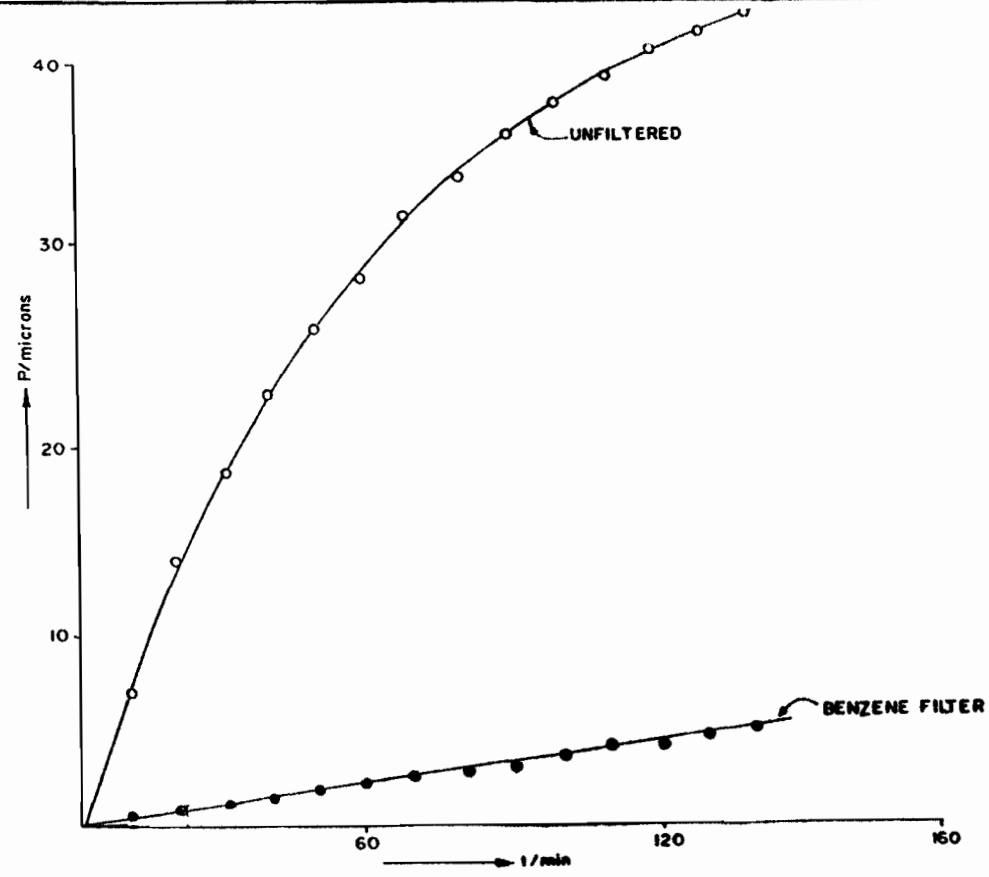

Fig. 3 PLOT OF Pvst FOR UNFILTERED AND FILTERED PHOTOLYSIS OF SAMPLE NHA3 AT 298 K

vacuum line (figure 1). The quartz window of the cell is covered with the benzene filter before the UV lamp is switched on for radiation to fall on the sample. The light source used is a high pressure mercury arc lamp (HRK 125W, Philips, Holand). The spectral distribution of the light source is given in ***table I.*** The pressure of nitrogen accumulated over the sample during irradiation (measured with a Mcleod Gauge) was recorded as a function of time.

RESULTS AND DISCUSSION

The intensity of light emitted by the full source of light was obtained by determining its actinometry using potassium ferri oxalate as a standard. (Sood and Standley, 1990). The values of absolute intensity quoted by them were used for all photodecomposition and photolysis studies of the azide (Irom, 1990). The values are presented in ***table I.***

TABLE 3 PHOTODECOMPOSITION OF SAMPLE AT DIFFERENT TEMPERATURES THROUGH BENZENE FILTER AND AT I_3

Time (mins)	Pressure (microns)			
	P_{298K}	P_{288K}	P_{273K}	P_{267K}
10	0.612	0.437	0.350	0.175
20	1.050	0.875	0.710	0.438
30	1.575	1.225	1.050	0.700
40	2.188	1.575	1.400	0.950
50	2.625	2.015	1.823	1.125
60	3.150	2.450	2.155	1.350
70	3.675	2.775	2.625	1.575
80	4.025	3.225	3.050	1.750
90	4.375	3.650	3.450	2.013
100	4.725	4.112	3.850	2.275
110	4.725	4.550	4.200	2.450
120	5075	4.812	4.550	2.800

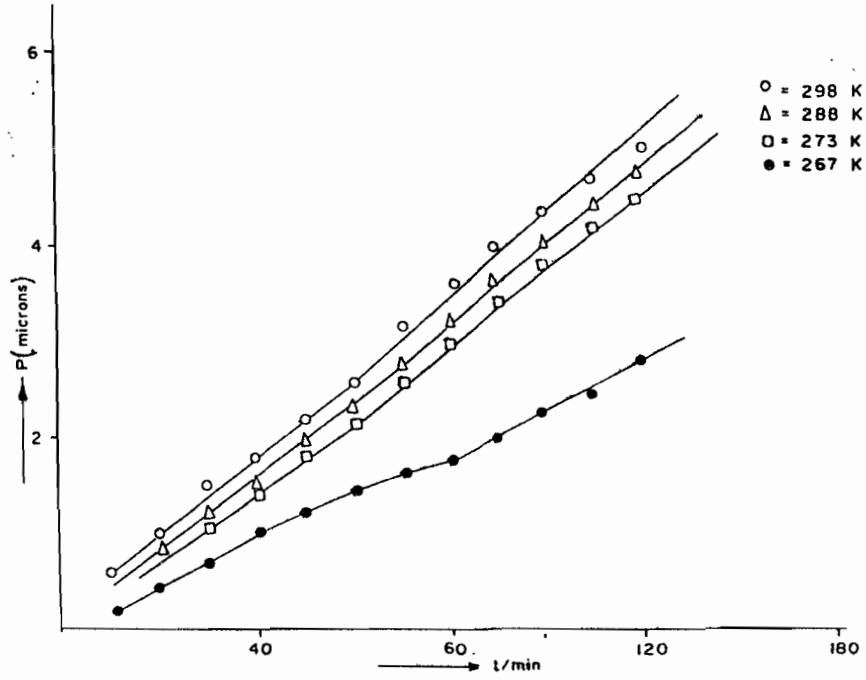

Fig. 4a PLOT OF P vst FOR THE PHOTO DECOMPOSITION OF SAMPLE NHA3 AT DIFFERENT TEMPERATURES THROUGH BENZENE FILTER AT I_3

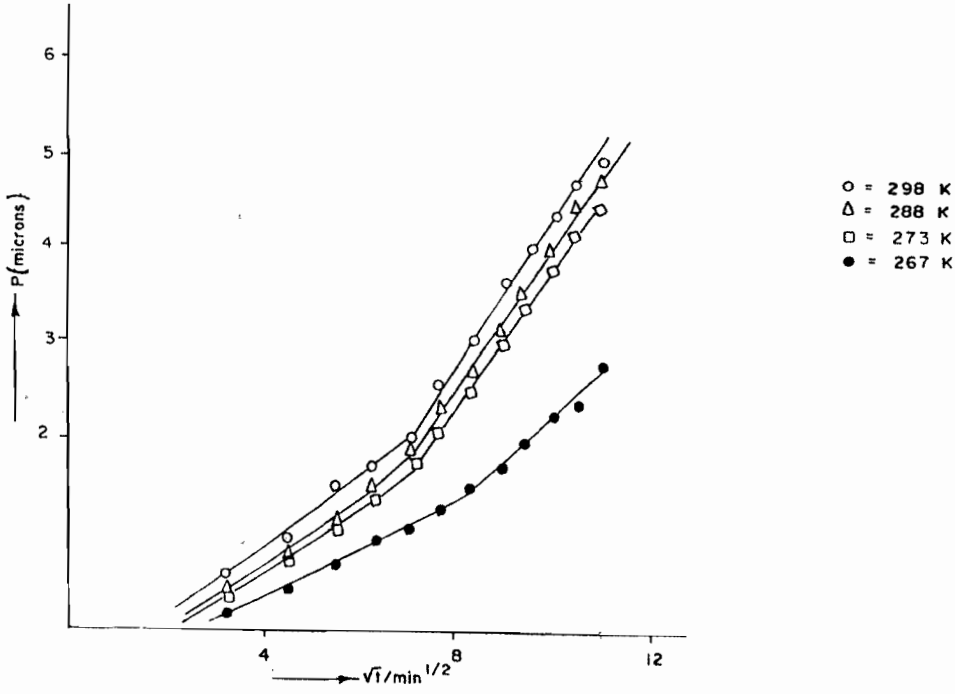

Fig. 4b PLOT OF P vs $\sqrt{t}$ FOR THE PHOTO DECOMPOSITION OF SAMPLE NHA3 AT DIFFERENT TEMPERATURES THROUGH THE BENZENE FILTER AT I_3

The p-t data for the photodecomposition of nickel hydroxy azide with unfiltered radiation is compared with that of filtered radiation as shown in table 2 and plotted in figure 2. Although the average transmission through the benzene filter is only about 50% in the wavelength region, 289-350nm, the appreciable rate of photolysis suggest that the wavelengths in the region 280-330nm could be photolytically active. This confirms the observation in the diffuse reflectance spectra of nickel hydroxy azide (fig 5), consistent with the appreciable photolysis rate of the azide through benzene filter in figure 3. The slight photolysis is therefore mostly due to wavelengths between 289-350nm within which benzene filter has 50% transmission. The p-t data for photodecomposition of the azide at different temperatures is presented in table 3. The plots of p vs t and p vs $\sqrt{t}$ are shown in figs 3 and 4.

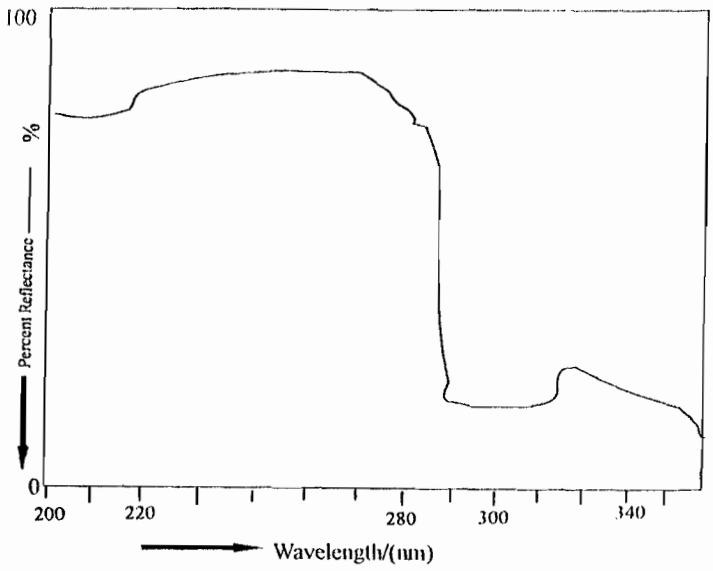

Fig. 5 DIFFUSE REFLECTANCE SPECTRA OF NICKEL HYDROXY AZIDE. ABSORPTION OCCURS BETWEEN 210 AND 260nm.

The p-t cure of photodecomposition through benzene filter shows acceleratory period after an initial spurt of gas as seen in fig. 4 at low intensities. This behaviour is similar to that shown by the photolysis of barium azide using unfiltered UV light (Yoganarasimhan et al, 1967). One of the mechanisms suggested by them involves the concept of deep surface traps for the mobile excitons in the azide lattice. The greater the concentration of surface imperfections and deeper surface levels, the less chances of an interaction between two excitons trapped or otherwise. So in the initial stages the possibility of bimolecular decomposition of excitons is less than after all the deep traps are filled. This explains the observed accelerating rate and increasing accelebratory rate with decreasing decreasing intensity of radiation.

In the present investigation of photodecomposition of nickel hydroxy azide, the acceleratory period is observed only when the photodecomposition is performed through a filters. The benzene filter cuts off most of the more actinic wavelengths lower than 280nm (Benzene absorbs all wavelengths lower than 280nm and has a maximum transmission of 50% at λ>280nm). A very small intensity of radiation thus reaches the sample with lesser penetration into the interior of the solid.

The situation reveals that the initial stage of predominantly surface reaction occurs with a rate which accelerates when all the available deep surface traps are filled. In the case of unfiltered photolysis of nickel hydroxy azide (Irom, 1990), the acceleratory period is not observable. Probably all the surface traps in this case get filled almost instantaneously and the photolysis proceeds with too high a rate to allow any deactivation to be observed.

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