

PHOTOLYSIS OF THE AZIDE ION IN AQUEOUS SOLUTIONK. TENNAKONE*, O. A. ILLEPERUMA**, S. PUNCHIHEWA,
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Abstract : The photolysis of the azide ion in an aqueous medium purged with argon is found to generate ammonia and nitrogen whereas oxygen purged solutions generate nitrite and nitrogen. Quantum yield measurements are given and possible reaction mechanisms are suggested.

1. Introduction

The kinetics of the decomposition of inorganic azides in solid state have received considerable attention.^{4,7,9} In vacuum all azides decompose into metal and nitrogen, the decomposition can be brought about by heat, light, shock or ionizing radiation. Heavy metal azides in solid state show absorption edges in the vicinity of 300-400 nm. The photochemical decomposition of heavy metal azides is believed to originate from band gap excitations which generate electron-hole pairs.⁹ However, in the case of alkaline metal azides the excitonic absorption in the region 140-150 nm is known to cause the decomposition.⁹ According to Beckman and Dickinson,¹ the photolysis of hydrogen azide solution yields gaseous nitrogen, ammonia, hydrazine and hydroxylamine. Nosaka *et al.*^{5,6} have reported that photolysis of azide ion (aqueous medium) in the presence of semiconductor catalysts produce ammonia and nitrogen. However, they have not compared the yields in the absence and presence of semiconductor catalysts. We have carefully examined the photolysis of azide ion in the presence and absence of semiconductor catalysts and found that the photodecomposition of azide ion in aqueous medium is not influenced by semiconductor catalysts. The only detectable products in the photolysis of argon purged solutions were ammonia and nitrogen. Photolysis of oxygen purged solutions yielded nitrite ion and nitrogen.

2. Experimental Method

Photolysis experiments were carried out in a double walled photochemical reactor (Applied Photophysics) made from borosilicate glass. The central

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axis of the cylinder is fitted with a 400W medium pressure Hg lamp. A facility is also provided for the insertion of cylindrical glass filters. 350 ml of sodium azide solution was continuously irradiated and aliquots of solution drawn at different intervals of time were tested for ammonia (indophenol blue method³) hydrazine (p-dimethylaminobenzaldehyde method⁸) and hydroxylamine (potassium iodate resorcinol reagent²). All these estimations were carried out spectrophotometrically. Before irradiation, solution was rapidly purged with purified argon. The gas in the atmosphere of the reactor and in the solution was analysed for nitrogen, oxygen and hydrogen by gas chromatography (Shimadzu model E6-9AM). An International light IL 700 radiometer was used for the measurement of light intensities. The absorption spectrum of the azide solution was recorded using a Shimadzu UV-3000 spectrophotometer.

3. Results and Discussion

In argon purged solutions the only detectable products of photolysis were ammonia and nitrogen (hydrazine and hydroxylamine were absent or less than 10^{-6} M). Figure 1 indicates the yield of ammonia as a function of time. The absorption spectrum of the sodium azide solution shows a sharp edge (Figure 2) at ~ 280 nm. Photodecomposition is seen to occur only if the irradiation wavelength is $\lesssim 280$ nm (when a filter that cuts off light of wavelength ~ 300 nm was used, the decomposition did not take place). The quantum yields of ammonia and nitrogen at $\lambda = 265$ nm (the significant emission in the lamp at $\lambda < 300$ nm is 265 nm and the intensity at this wavelength estimated using a monochromator is $\sim 4.9 \times 10^{16}$ photons s^{-1}) was estimated to be 5.3, 18.6 % respectively.

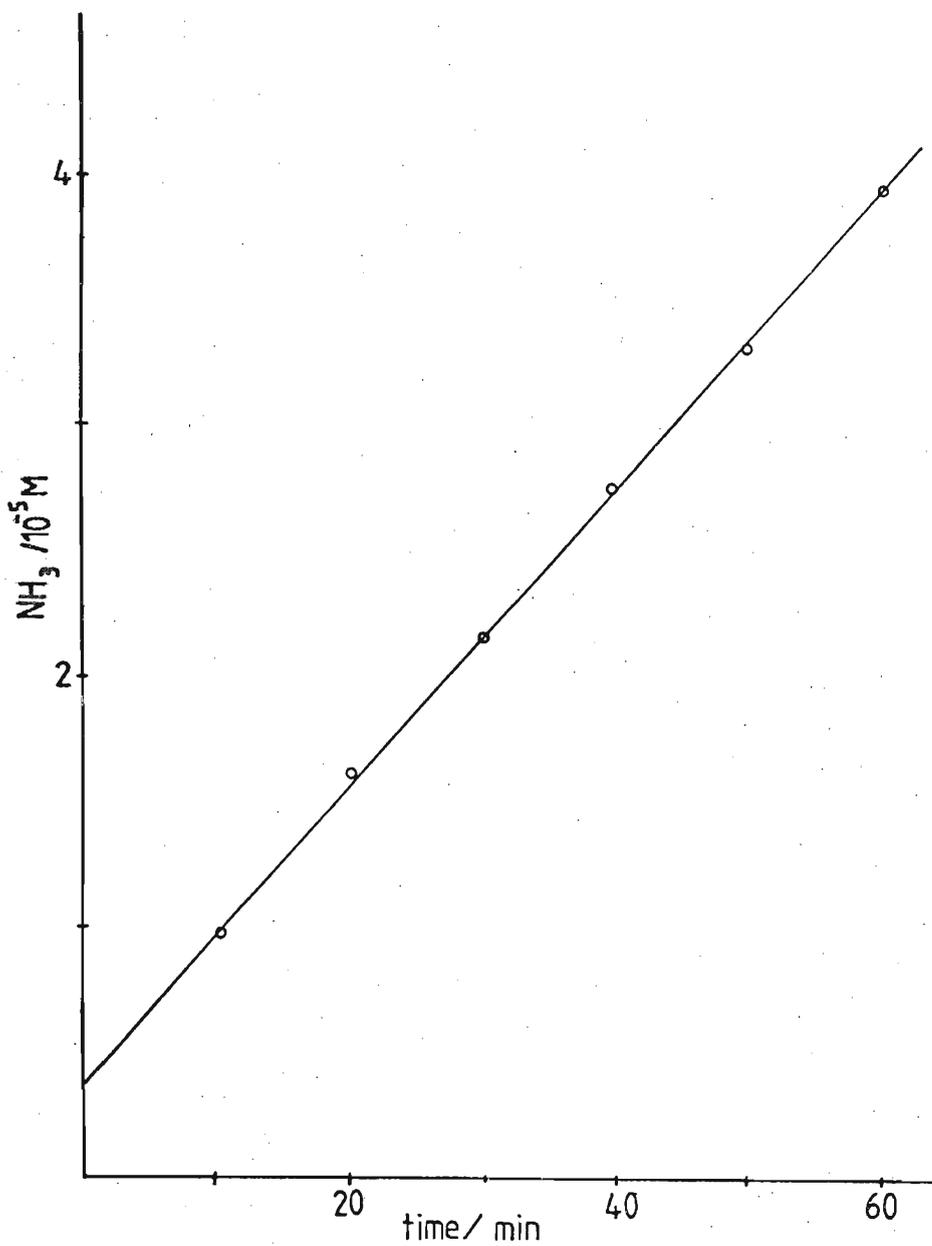


Figure 1. Time variation of the ammonia yield in an argon purged solution (Initial concentration azide $2.2 \times 10^{-4} \text{ M}$)

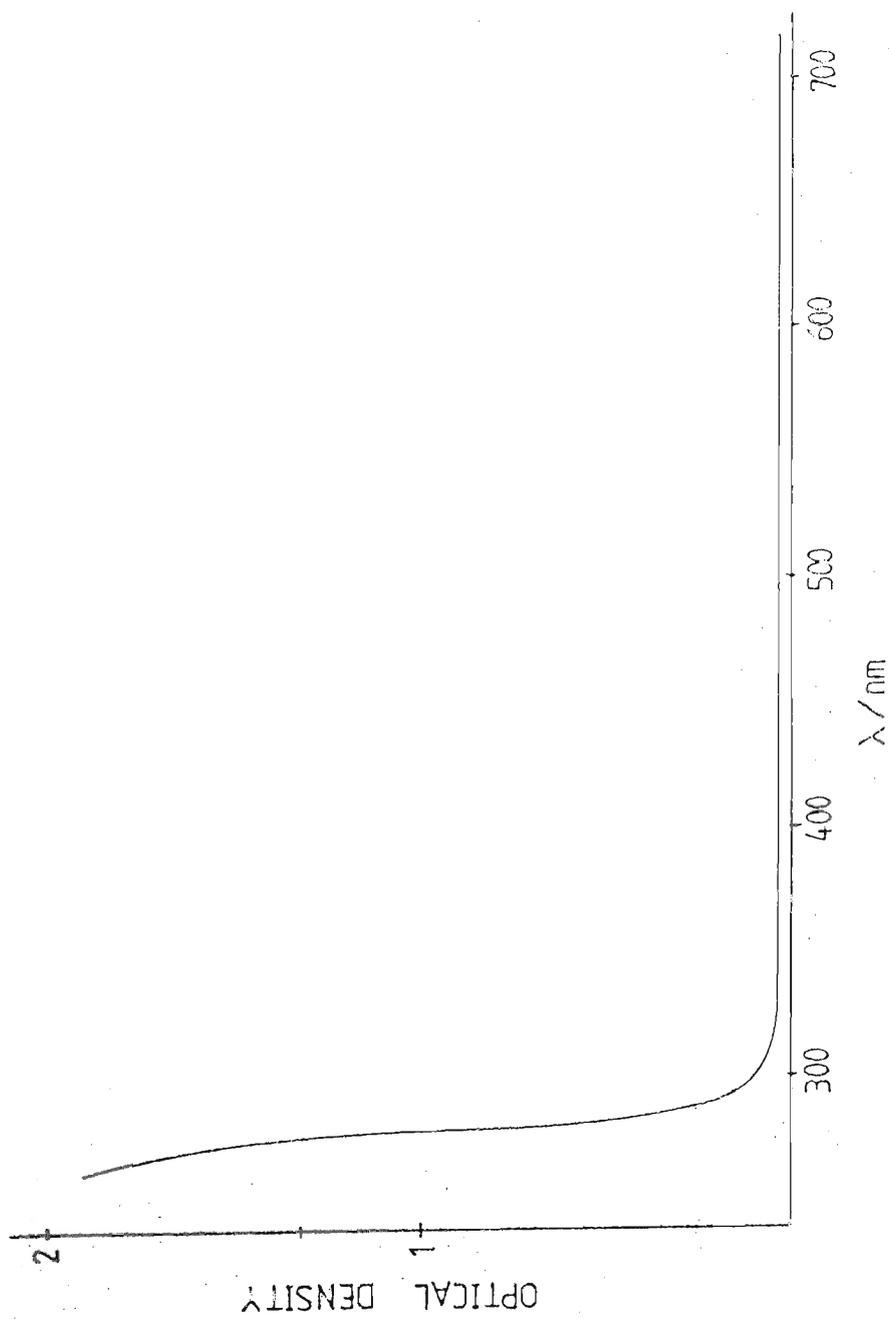


Figure 2. Absorption spectrum of a 2×10^{-4} M solution of sodium azide

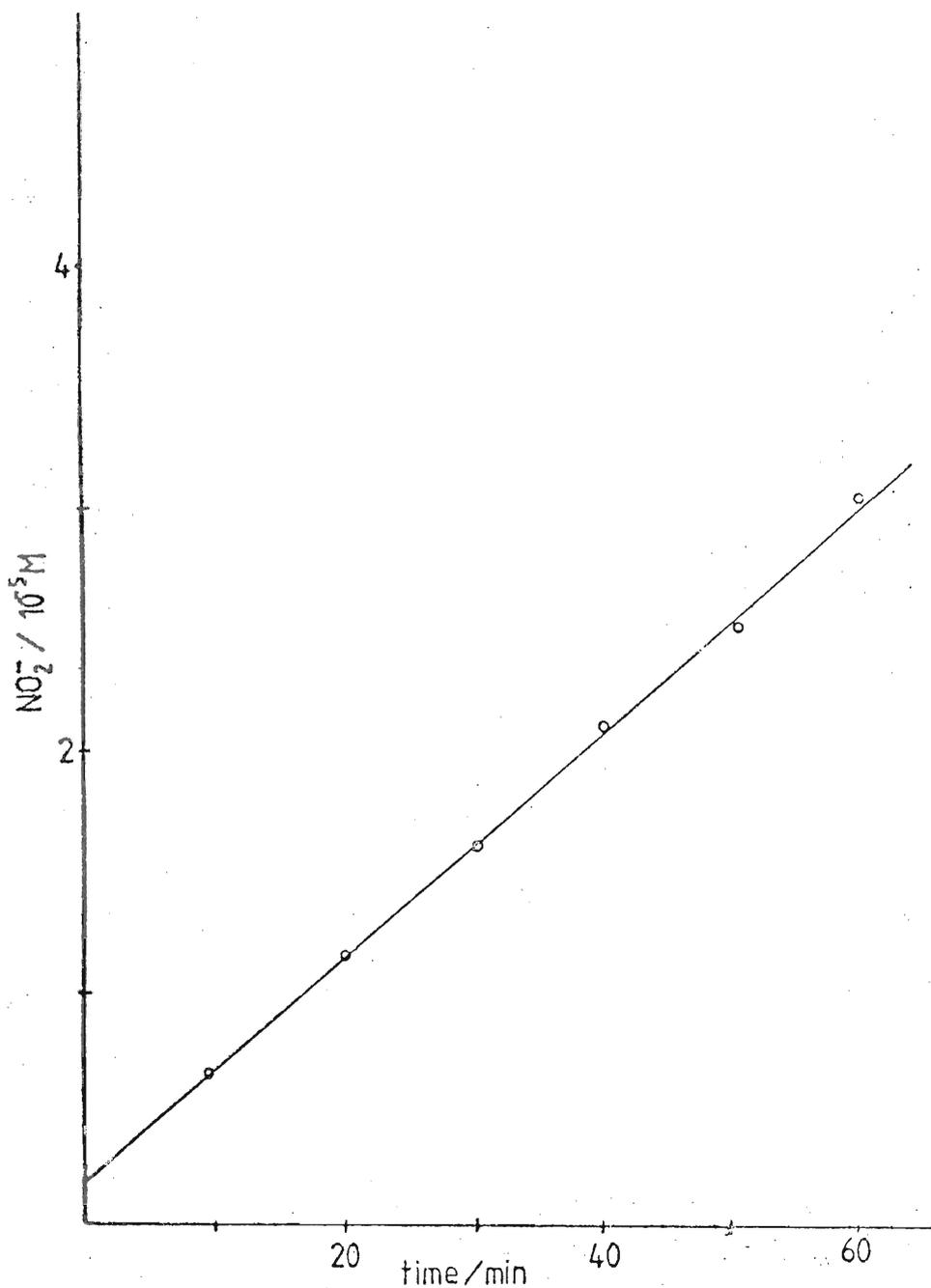
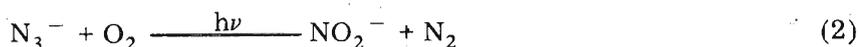
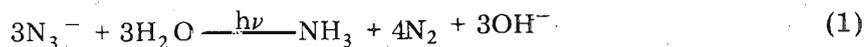


Figure 3. Time variation of the nitrite yield in an oxygen purged solution (Initial concentration of azide = $2.2 \times 10^{-4} \text{ M}$)

When the solution was purged with O₂ (160 ml min⁻¹) the products of photolysis were nitrite and nitrogen with barely detectable amounts of ammonia. The quantum yields of nitrite, nitrogen were found to be 41, 4.7 % respectively. Semiconductor photocatalysts did not have any influence on yields or the products of photolysis. Again, in both cases (ammonia production in argon purged solution and nitrite production in oxygen purged solution) were found to be insensitive to changes in pH. The photochemical reactions occurring can be summarized as follows:



The observed ratios of the quantum yields (NH₃:N₂ ~ 1 : 3.5, NO₂⁻ : N₂ ~ 1 : 1.1) agrees with (1) and (2). The insensitivity of the reaction to pH and the presence of semiconductor catalysts suggests that the primary step in photolysis does not involve charge transfer from azide to H⁺ ions, but instead the excited azide ion or an intermediate product of its decomposition directly interacts with water molecules or oxygen.

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