

PHOTOLYSIS OF AZIDES IN GLASSY SOLUTIONS: SPECTRAL AND PHOTOCHEMICAL PROPERTIES OF NITRENES

S. B. BRICHKIN, V. A. SMIRNOV and M. V. ALFIMOV

Institute of Chemical Physics, Academy of Sciences, 142432 Chernogolovka, Moscow Region (U.S.S.R.)

T. P. NAYDENOVA and L. F. AVRAMENKO

Kiev State University, 252017 Kiev (U.S.S.R.)

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Summary

The spectral and photochemical properties of nitrenes formed during the photolysis of aromatic azides in rigid solutions at 77 K were investigated. The T_1 - T_0 fluorescences of 4-biphenyl nitrene and 4,4'-biphenyl dinitrene were observed. A photoreduction of the nitrenes in rigid solutions at 77 K was found. The excited nitrene was shown to react with the matrix to form a substituted amine.

1. Introduction

In recent years the aromatic azides have received considerable attention mainly because of their use as the photoactive elements in photoresist systems [1]. The photodecomposition of azides results in the elimination of nitrogen and the formation of nitrenes which then react with the solvent. The optical absorption of the aromatic nitrenes at 77 K has been observed by Reiser and coworkers [2, 3], but the luminescence and the photochemical properties have not been elucidated. In this work we report some new results for phenyl and biphenyl nitrenes.

2. Experimental

The photolysis of the aromatic azides was carried out either in a methanol-ether (1:1) glass or in a methylcyclohexane glass (10^{-2} - 10^{-4} M) at 77 K. The samples were irradiated by 1 kW mercury or xenon arc lamps which were filtered with appropriate sets of glass and/or interference filters. Absorption spectra were obtained with a Unicam SP-800 spectrophotometer and luminescent measurements were carried out using the spectrofluorimeter described in ref. 4. The lifetimes of the nitrene fluorescences were measured

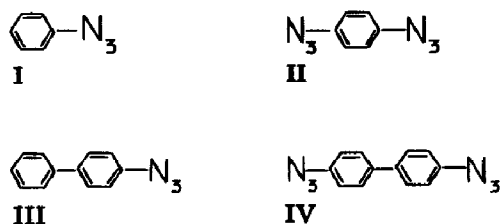


Fig. 1. The structures of the azido compounds: I, phenyl azide; II, *p*-phenylene diazide; III, 4-biphenyl azide; IV, 4,4'-biphenyl diazide.

with stroboscopic equipment [5]. The azido compounds are shown in Fig. 1. Compounds I - IV were synthesized by azotizing the corresponding amines and diamines.

3. Results

The photolysis of the aromatic azides results in the formation of the corresponding nitrenes. Their absorption spectra which are shown in Fig. 2 are similar to those reported by Reiser and coworkers [2, 3]. On UV irradiation at 77 K the dinitrenes are formed from the diazides in two steps with the corresponding azido nitrenes as intermediates. For example, the absorption spectrum of 4,4'-biphenyl diazide after intense but short irradiation of the sample is shown in curve 2 of Fig. 2(b). The absorption at 350 nm is thought to be due to the azido nitrene which is formed with a quantum yield ϕ_1 of 0.4 [6]. On irradiation at 365 nm the azido nitrene is transformed into the dinitrene with a quantum yield ϕ_2 of 1.0 [6]; however, the absorption band of 4,4'-biphenyl diazide shows no change. Prolonged irradiation of the sample at 300 nm leads to the complete transformation of 4,4'-biphenyl diazide into 4,4'-biphenyl dinitrene (curve 3 of Fig. 2(b)). The same behaviour was also found for *p*-phenylene diazide.

In general the absorption spectra of nitrenes and dinitrenes have an intense short wavelength band, a much weaker long wavelength band and pronounced vibronic structure. Therefore it is concluded that the biphenyl groups of the nitrene and dinitrene molecules are more planar than those of the parent azide molecules. This is probably due to the strong conjugation of the phenyl rings in the nitrenes studied.

3.1. Luminescent properties of nitrenes

The luminescence spectra of 4-biphenyl nitrene and 4,4'-biphenyl dinitrene at 77 K are shown in Fig. 2 (Fig. 2(a), curve 5; Fig. 2(b), curve 4). It was observed that (1) the luminescence increases with the growth of the absorbance peak of the nitrene, (2) the excitation spectrum of luminescence is coincident with the corresponding absorption spectrum and (3) the luminescence disappears on warming.

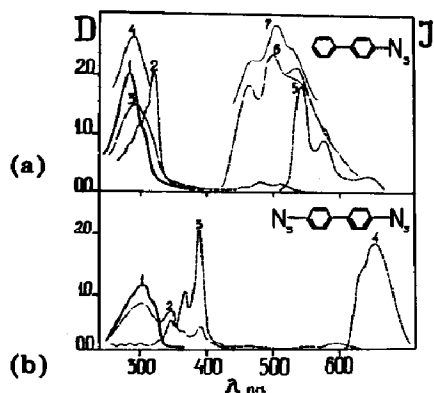


Fig. 2. (a) Absorption spectra in a methanol-ether matrix at 77 K of: curve 1, 4-biphenyl azide; curve 2, 4-biphenyl nitrene; curve 3, the product of nitrene photoreduction; curve 4, 4-biphenyl amine. Luminescence spectra under the same conditions of: curve 5, 4-biphenyl nitrene; curve 6, the product of nitrene photoreduction. Curve 7, the phosphorescence spectrum of 4-biphenyl amine. (b) Absorption spectra in a methanol-ether matrix at 77 K of: curve 1, 4,4'-biphenyl diazide; curves 2 and 3, 4,4'-biphenyl diazide after short (2) and prolonged (3) UV irradiation. Curve 4, fluorescence spectrum of 4,4'-biphenyl dinitrene under the same conditions.

Since the ground states of the nitrenes [7] and of the quinoid structures of the dinitrenes [8] are triplets, it is concluded that the observed emission is the fluorescence which is caused by the T_1-T_0 transition. The locations of the T_1 levels are estimated to be

$$E_{T_1} = 2.35 \pm 0.02 \text{ eV} \quad \text{for 4-biphenyl nitrene}$$

$$E_{T_1} = 2.01 \pm 0.02 \text{ eV} \quad \text{for 4,4'-biphenyl dinitrene}$$

The fluorescence lifetimes of 4-biphenyl nitrene and 4,4'-biphenyl dinitrene are 2 and 18 ns respectively. It is known [9] that 1-pyrene nitrene fluoresces and it can be assumed that luminescence is a universal property of aromatic nitrenes with a rather large aromatic basis. We did not observe any luminescence in phenyl nitrene or in *p*-phenylene dinitrene (*i.e.* the quantum yield q of emission was less than 10^{-3}). The high rate of the non-radiative processes is due to a significant distortion of the phenyl ring from a planar conformation by the non-bonding electrons on the nitrogen. The locations of the T_1 levels for phenyl nitrene and *p*-phenylene dinitrene were determined from their absorption spectra:

$$E_{T_1} = 2.48 \pm 0.05 \text{ eV} \quad \text{for phenyl nitrene}$$

$$E_{T_1} = 2.50 \pm 0.05 \text{ eV} \quad \text{for } p\text{-phenylene dinitrene}$$

3.2. Photochemical properties of nitrenes

The prolonged irradiation of nitrenes results in further phototransformation. The changes in the absorption spectrum of 4-biphenyl nitrene caused

by irradiation within the long wavelength absorption band (400 - 500 nm) are shown in Fig. 2(a). It can be seen that the irradiation leads to the disappearance of the nitrene absorption band at 315 nm (curve 2) and to the appearance of a new absorption band at 290 nm (curve 3). The emission spectrum changes in a similar way; the nitrene fluorescence disappears and the phosphorescence of a new product appears and increases (Fig. 2(a), curves 5 and 6). The new absorption and phosphorescence spectra are similar to those of 4-biphenyl amine (Fig. 2(a), curves 4 and 7). This leads us to conclude that photoreduction of the nitrene occurs in the reaction of the excited nitrene with the solvent at 77 K. It should be noted that the spectra of the new product differ slightly from those of 4-biphenyl amine and we assume that a substituted amine may be formed in this reaction. The photoreduction quantum yield ϕ_r of nitrene was found to be equal to 0.02 ± 0.005 in a methanol-ether matrix at $\lambda_{ex} = 313$ nm. The photoreduction also takes place in a hydrocarbon (methylcyclohexane) matrix, but the quantum yield is somewhat smaller. This is probably due to the greater energy of the C-H bond in the hydrocarbon compared with that in the alcohol. The photoreduction of the dinitrenes results in the formation of the corresponding substituted diamines.

The photoformation of amine (diamine) from nitrene (dinitrene) may proceed in two ways: (1) by abstraction of two hydrogen atoms from the solvent; (2) by insertion or pseudo-insertion into the C-H (or O-H) bonds of the solvent. Additional experiments were carried out in order to elucidate the mechanism, and the results are shown in Fig. 3. The irradiation of 4,4'-biphenyl dinitrene within the range 400 - 600 nm results in photoreduction of the dinitrene and the formation of the corresponding diamine (Fig. 3, curve 3). Subsequent irradiation of the sample leads to the appearance of cation radical amine absorption bands at about 450 nm. Comparison of this cation radical amine absorption spectrum with those of the cation radicals of

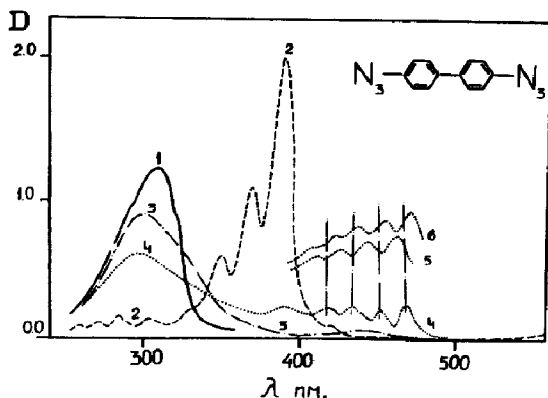
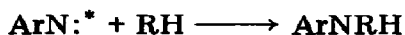
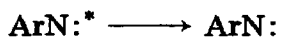
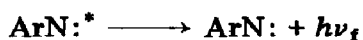
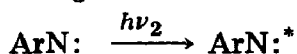
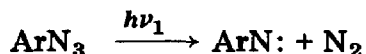


Fig. 3. Absorption spectra in a methanol-ether matrix at 77 K of: curve 1, 4,4'-biphenyl diazide; curve 2, 4,4'-biphenyl dinitrene; curve 3, the product of dinitrene photoreduction; curve 4, the same product after UV irradiation. Cation radical absorption spectra under the same conditions of: curve 5, benzidine; curve 6, tetramethylbenzidine.

tetramethylbenzidine and of benzidine show that the peaks are situated between the corresponding peaks of the cation radicals of the non-substituted and the tetramethyl-substituted amines. The well-resolved structure implies that photoreduction of the nitrenes results in the formation of only one compound, the substituted amine, and not in a mixture of different amines. Therefore it is concluded that the formation of the amine from the excited nitrene at 77 K proceeds by insertion of the excited nitrene into the C—H (or O—H) bonds of the matrix, and not by the successive abstraction of two hydrogen atoms. It must be noted that the insertion into C—H bonds is peculiar to the singlet nitrene. We believe that secondary amines in glasses are formed from the triplet nitrenes by the abstraction of a hydrogen atom and the formation of two radicals, followed by radical recombination after spin relaxation. Such a mechanism has been called "pseudo-insertion" [10]. However, it should be noted that the irradiation of phenyl nitrene did not result in the formation of aniline in an appreciable amount. Apparently competition between photoreduction and photorearrangement of the nitrene to azepine occurs. For example, the photorearrangement process of 2-biphenyl nitrene to carbazole is known [11]. Finally, it should be noted that the absorption spectrum of the substituted *p*-biphenyl amine cation radical has been erroneously attributed [3] to the cation nitrene.

4. Conclusion

The following general scheme of aromatic azide photolysis is proposed:



The results obtained may be important in studies of the photoreactions of aromatic azides in plastic media.

Acknowledgment

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