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Spectroscopic investigation of some aromatic azides

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The electronic absorption spectra of some aromatic azides based on 4,4'-diaminobiphenyl or 4,4'- diaminobenzophenone, etc. Were discussed in terms of the primary products and the mechanism of photolysis reactions of azides. The progress of the photochemical reactions was monitored by means of the optical absorption spectra. It was found that the photolysis of biphenyl azide in solution develops the first-order kinetics model. Thin azoaromatic polymer films were obtained by the photolysis of aromatic azides in vacuum.

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1. Introduction

Aromatic azides receive a continuous interest because of their useful applications in photoresist compositions, photoaffinity labelling, preparative heterocyclic chemistry, surface modification of polymers and metals, preparation of conducting polymers etc. [1-10]. It is known that these compounds decompose by UV radiation or heating, yielding highly reactive nitrene intermediates which can undergo a multitude of reactions such as dimerization, attack on heteroatoms, addition to multiple bonds, insertion into a C-H, N-H or O-H bonds, proton abstraction, reaction with molecular oxygen, ring expansion. The ground state of the most aromatic nitrene radicals is a triplet. The short-living thermodynamically unstable singlet species can pass by intersystem crossing mechanism into triplet nitrenes [3, 10, 11].

$$R - N_3 \xrightarrow[\text{nitrene}]{h\nu,\ \Delta} R - N: + N_2$$

Also, photolysis of aromatic azides has attracted attention due to the complexity of the reaction mechanism. The reactions of nitrene radicals in solution or polymer matrices depend on the structure of azide, solvent or polymer, on the one hand, as well as on the layer morphology in which the nitrene radical was generated. Often the resulting products are difficult to be characterized, they being insoluble and tarry materials.

Most of the measurements of the nitrene characteristics have been made at low temperature or in rigid matrices, where these reactive intermediates are rather stable [3, 12, 13]. Photolysis studies of aromatic azides at room temperature are few in number and can provide a better understanding of the nitrene chemical reactivity.

In this paper, the photodecompostion of some aromatic diazides in solution at room temperature using electronic absorption spectroscopy is discussed. Based on these diazides, thin transparent films of azoaromatic polymers were obtained.

2. Experimental

Aromatic diazides such as 4,4'-diazidobiphenyl, 4,4'diazidobenzophenone were prepared from the corresponding diamines by the reaction of the diazonium salts with sodium azide by conventional procedures [14-16]. The reaction products were purified by recrystallization. 2,6-Bis(4-azidobenzylidene)-4-methylcyclohexanone (ABC) was obtained from Aldrich and used without further purification. Dichloromethane (Aldrich) was of spectrophotometric grade.

The ultraviolet-visible absorption spectra were recorded in dichloromethane on a Specord M42 spectrophotometer using generally 10 mm quartz cells fitted with polytetrafluoroethylene stoppers. Dicholoromethane is considered to be rather inert to the nitrene radicals [3]. The irradiations were performed using a 350 w medium pressure mercury lamp at room temperature. The irradiating wavelenghts were set to correspond to the absorption maximum of the aromatic azides by using appropriate filters (302, 365 nm).

3. Results and discussion

The photolysis of aromatic azides was followed by ultraviolet-visible absorption spectroscopy, monitoring the modifications occurring in the absorption band intensity as a function the irradiation time.

The electronic absorption spectra of 4,4'-diazidobiphenyl, 4,4'-diazidobenzophenone and 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (ABC) are characterized by intense absorption bands in dichloromethane solution located at 297, 302 and 356 nm, respectively. These absorption bands are assigned to π - π^* electronic transition taking into account the spectra of initial compounds [17, 18]. During UV irradiation at long wave absorption bands, all diazides rapidly decomposed.

Fig. 1. displays spectral changes observed upon irradiation of 4,4'-diazidobiphenyl in dichloromethane solution. Simultaneously with the decrease in the intensity

of absorption band at 297 nm, a new absorption band appeared in the longer wavelength region at around 364 nm. Two isosbestic points at 263 and 323 nm were observed in spectral pattern. After 60 s of UV irradiation the absorption at 297 nm practically disappears and the isosbestic points become ever less defined. On continued irradiation the absorption band at about 360 nm shifts to shorter wavelenghts (350 nm). This blue shift depends on the azide concentration, solvent and irradiation intensity.

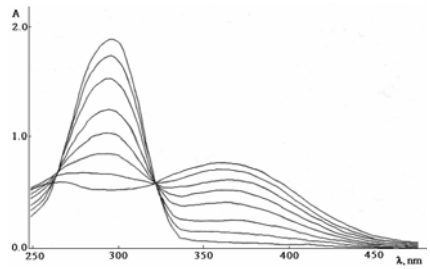


Fig. 1. Spectral changes upon irradiation of solution of 4,4'-diazidobiphenyl in dichloromethane; irradiation times: 0, 2, 5, 10, 15, 20, 30, 60 s.

The decrease in the absorption band intensity at 297 nm suggests the photolysis of azido groups and the generation of nitrene radicals. The new absorption band can be presumably due to the reaction products of dinitrene and rearranged intermediates with the oxygen [19-21]. At high concentration of biphenyldiazide, this absorption band is located at about 375 nm and it can be assigned to an azo-compound due to nitreno-nitreno and azido-biphenylnitrene reactions.

The absorbance decay of 4,4'-biphenylazide during photolysis can be expressed by a first-order relation according to the expresion:

$$\ln(A_o - A_\infty)/(A_t - A_\infty) = kt$$

where A_o, A_∞ and A_t are the absorbances at initial, final and t times, respectively and k is the rate constant. The experimental data (A, t) are plotted for 4,4'-bisphenylazide in Fig. 2.

The value of the rate constant was estimated from the first order plot being 8.6×10^{-2} s^{-1}.

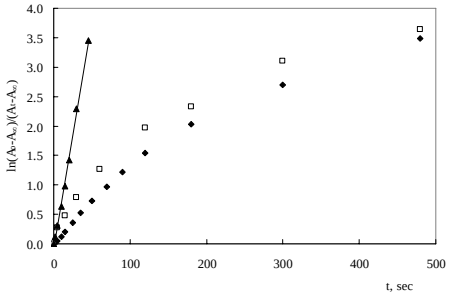


Fig. 2 Plots $\ln(A_o - A_\infty)/A_t - A_\infty)$ vs. irradiation time for aromatic diazides; 4,4'-diazidobiphenyl (◢), 4,4'-diazidobenzophenone (□), ABC (◆).

Remarkable absorption spectrum changes were occurred upon UV irradiation of 4,4'-diazidobenzophenone solution in dichloromethane. Also, the absorbance at 302 nm decreases with the increasing of irradiation time (Fig. 3). There are three isosbestic points at 242, 273 and 322 nm, respectively, but the two last points were gradually change and become less defined. A transformation degree of 0.70 was observed after 480 s of irradiation. In the case of a dilute solution of 4,4'-diazidobenzophenone in dicloromethane the following absorption bands were observed at about 315 and 274 nm, respectively, after 30 min of UV irradiation, while for concentrated solutions (> 10^{-3} mol/l) in presence of oxygen, the absorption bands at about 345 and 270 nm appeared. The absorption band at 345 nm can be ascribed to 4,4'-dinitrobenzophenone [22]. The tail beyond 360 nm may arise from azo compounds.

The photochemical behavior of this diazide is more complex because reactions at the excited state carbonyl group can occur. The deviation from first-order kinetics evidences the complexity of photolysis process (Fig. 2).

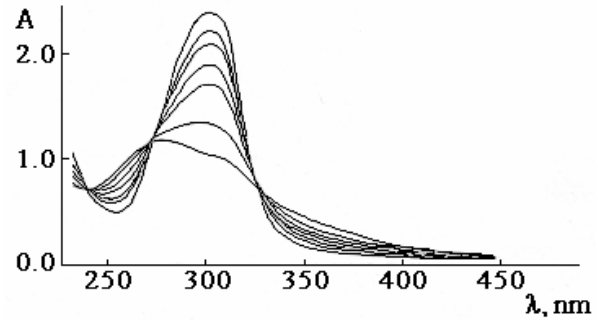
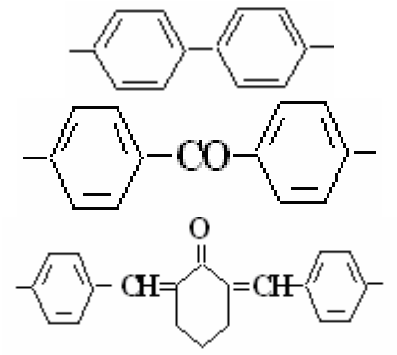


Fig. 3 UV-Vis spectral changes during photolysis of ,4'-diazidobenzophenone in dichloromethane solution, irradiating times: 0, 10, 15, 25, 35, 70, 120 s.

Upon photoirradiation, the absorption band at 356 nm of the azide groups in ABC decreased with the increase of irradiation time. The absorption spectra show an absorbance increasing in the range 395-490 nm, with isosbestic points at 315 nm and 388 nm, respectively, whereas the absorption maximum at 356 nm shifted to longer wavelenghts This red shift of the absorption maximum can be due to the coupling reaction of nitrenes leading to the formation of azo compounds, but other intermediates can exist in reaction system. Usually, the red shift of azide maximum is characteristic to irradiation under nitrogen atmosphere [23], when the formation of azo product is favored. The transformation degree of azido groups during photolysis was 0,42 after irradiation for 480 s. In the later stages of the irradiation the isosbestic points did not maintain in the spectra. The photolysis kinetics for ABC did not obey a first-order relation (Fig. 2).

The aromatic diazides were applied to obtain thin films of azoaromatic conjugated polymers. Such polymer films have been obtained by a chemical vapor deposition (CVD) procedure using photochemical decomposition of

aromatic diazides in vacuum. The reaction of nitrene radicals with an azido group or the nitrene recombination lead to the formation of azoaromatic products. The resulting polymers have the following structure: - Ar – N = N -, where Ar =



The thin transparent films based on 4,4'-diazidobiphenyl display absorption bands at about 200 and 400 nm, respectively (Fig. 4). The absorption band around 400 nm can be attributed to azoaromatic structures. Thicker and less transparent polymer films show an additional absorption band at about 310 nm which is assigned to branching amine structures resulted by the reaction of nitrene insertion into C-H bonds [3,10].

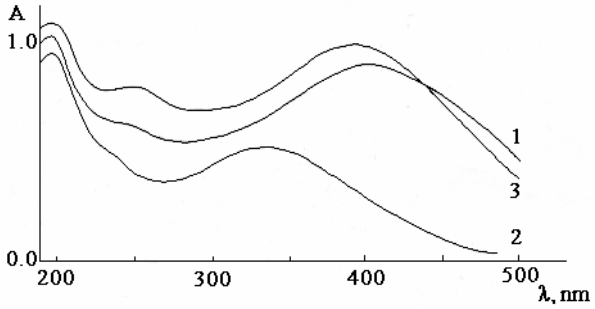


Fig. 4. Electronic absorption spectra of polymer films resulting from photolysis of aromatic diazides; 1-diazidobiphenyl, 2-diazidobenzophenone, 3-ABC

The poly(azobiphenyl) films were insoluble in organic solvents. In concentrated sulfuric acid the polymer film becomes rapidly deep blue in color due to the protonationof azo bonds and the absorption band at 400 nm is shifted to 560 nm (Fig. 5). This spectral behavior is reversible. However, the poly(azobiphenyl) films are not completely soluble in concentrated sulfuric acid, although polykis-azobenzenes obtained from photolysis of 1,4-diazido-azobenzene dissolve well in sulfuric acid [24]. The sulfuric acid soluble fraction shows absorption at about 600 nm and this fact suggests the presence of conjugated azoaromatic sequences longer than three units in the polymer chain [24].

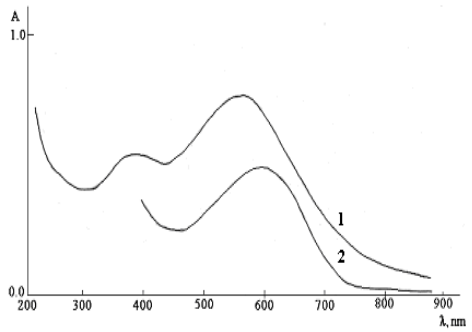


Fig. 5. UV-Vis absorption spectra of a poly(azobiphenyl) film; exposed to H_2SO_4 (1) and of the soluble fraction in H_2SO_4 (2).

The difference between the absorption spectra of polymer films derived from 4,4'-diazidobiphenyl and 4,4'-diazidobenzophenone can be explained by the break of π-electron conjugation due to the carbonyl groups.

The insolubility of the azobiphenyl polymers could be explained by a closed packing of the azoaromatic chromophore moieties, and such a packing arises from the coplanarity of the two phenyl rings that is better in nitrene molecules than in the parent azide leading to a strong conjugation of the phenyl rings in the nitrenes.

The surface morphology of the polymer films was investigated by atomic force microscopy (AFM) observations. The AFM 3D images for an azoaromatic polymer film deposited on quartz substrate is presented in Fig. 6.

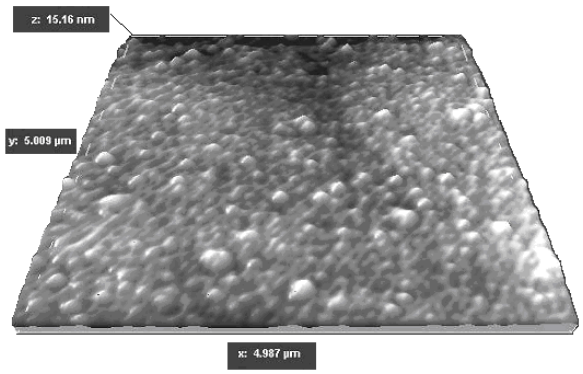


Fig. 6. AFM image of an azoaromatic polymer film on quartz substrate.

A smooth surface was evidenced over scanning range with a root mean square roughness of 6 nm and an average value of 6 nm. The deposited film on quartz is smooth, homogeneous and do not exhibit any pinholes.

4. Conclusions

The spectral pattern of the photolysis products of aromatic diazides reveals the multitude of reactions in which the nitrene redicals are implied in correlation with azide structure and irradiation conditions. On the other

hand, it was possible to obtain predominant azoaromatic polymers by promoting the azo-generating reactions in vacuum conditions.

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