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PHOTOLYSIS OF p-AZIDOANILINE IN APROTIC SOLVENTS

E. A. Pritchina, N. P. Gritsan,
and N. M. Bazhin

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In the photochemical conversions of aromatic azides [1, 2], azocompounds, primary and secondary amines, polymers, and other products formed as a result of dark conversions of nitrenes — primary products of the photoreaction — are formed. An investigation of the photolysis of aromatic azides in the presence of O_2 [3-6] showed that nitrenes in the triplet state, reacting with oxygen, form adducts, which are then converted to nitro compounds [3-5], the yield of which is low and does not exceed ∿20%. In [6] it was shown that the only primary photolysis product of azidobenzene in the presence of O_2 is nitroazobenzene.

The purpose of this work was to investigate the photochemical conversions of p-azidoaniline (I) in aprotic solvents and to establish the nature of the primary photolysis products and the pathways of their conversion in the presence of O_2.

EXPERIMENTAL

The photolysis of (I) was investigated in toluene, benzene, hexane, and CH_3CN. To record primary oxidation products, irradiation was conducted at 77°K in vitrifying matrices of methylcyclohexane or a mixture of toluene with THF (1:1 by volume). To investigate the dark conversions of the primary photolysis products, samples irradiated at 77°K were annealed in a thermostabilized stream of nitrogen. The temperature of annealing was maintained with an accuracy of ±1°C, and it was measured with a copper—Constantan thermocouple. The photolysis of (I) was studied in solutions with the natural content of O_2, saturated with O_2 and deoxygenated. Saturation was carried out in 30 min by bubbling O_2 through the solution at atmospheric pressure. For deoxygenation, Ar was bubbled through the solution for 30 min.

Photolysis was also conducted in Xe liquified at high pressure at 5.5°C (the temperature of thawing benzene) and CO_2, liquified at high pressure at ∿20°C: To obtain a solution of (I) in liquified gases, known amounts of Xe and CO_2 were refrozen into round quartz ampuls with an inner diameter of 2 mm, and outer diameter of 5 mm, and volume of ∿1 ml. In the case of Xe we worked at reduced temperature, since the critical temperature for Xe is 16.6°C [7]. After irradiation, the ampuls were opened at 77°K and thawed slowly, and after removal of gaseous Xe and CO_2, the products were analyzed.

Photolysis products of (I) in organic solvents were isolated by lyophilic sublimation of the solvent, since heating produced a resinification of the photolysis products. The products were separated on UV-254 Silufol plates from Kavalier in the MeOH—$CHCl_3$ (1:9) system. To identify the products we used mass spectrometry, PMR and UV spectroscopy, and

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Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk. Novosibirsk State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1749-1753, July, 1986. Original article submitted January 28, 1985.

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thin-layer chromatography with reference standards. Countersynthesis of the presumed photolysis product, p-nitrosoaniline (II), was carried out according to [8] from p-nitrosophenol, synthesized according to [9]. The ratio of the photolysis products was determined according to the UV absorption, eluting them from the Silufol plates with methanol.

The PMR spectra were recorded on a Varian XL-200 instrument at 20°C in $CDCl_3$. The chemical shifts were determined relative to TMS. The UV spectra were recorded on a Specord UV-VIS spectrophotometer; the mass spectra, on an LKB-2091 chromatograph/mass spectrometer, with an ionizing-electron energy of 70 eV. The ESR spectra were recorded at 77°K on a Bruker ER-200DSRS spectrometer at 9.75 GHz.

Toluene was freed of thiophenes by shaking with H_2SO_4, redistilled, and dried over Na [10]. Hexane was passed through a column with Al_2O_3, then redistilled. Benzene was purified according to [5] or by the method of double recrystallization according to [10]. For the purification of THF it was boiled with CuCl (0.4%) for 30 min and redistilled [11]. CH_3CN was preliminarily dried over $MgSO_4$ and redistilled over P_2O_5 [10]. Methylcyclohexane, produced by hydrogenation of toluene, was redistilled. Compound (I) was produced according to [12] in the processing group of the Scientific-Research Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR.

Compound (I) was irradiated with the light of a DRSh-500 lamp through a UFS-2 filter. To determine the quantum yield of photolysis, the 313-nm mercury line was isolated with a high-aperture-ratio monochromator, and the light intensity was determined with a ferrioxalate actinometer [13].

DISCUSSION OF RESULTS

Photolysis in the Absence of Oxygen. The photolysis of (I) was previously studied only in water [14]; the sole product of photolysis, p-benzoquinonediimine (an isomer of p-aminophenylnitrene), is obtained in the reaction of triplet p-aminophenylnitrene (III) with water [14].

In the irradiation of solutions of (I) in hexane and toluene at room temperature in the absence of O_2, compounds with an absorption spectrum in the visible region ($\bar{\nu}_{max}$ 25,400 cm^{-1} in toluene and $\bar{\nu}_{max}$ 27,000, 25,600 cm^{-1} in hexane) are formed. Chromatographic analysis shows that when solutions with a concentration of (I) no greater than 10^{-4} M are irradiated, the only photolysis product is 4,4'-diaminoazobenzene (IV). At a concentration of (I) $\sim 10^{-3}$ M, a substantial amount of high-molecular-weight products (resin) is also formed.

In the irradiation of (I) in glassy matrices at 77°K, a compound with characteristic absorption spectrum in the visible region and ESR spectrum consisting of a line at 6713 Oe (width Oe), typical of aromatic nitrenes in the triplet state [15, 16], is formed and stabilized.

When the irradiated sample is heated to 115°K, (III) in the triplet state disappears, and the final stable photolysis products — (IV) and p-phenylenediamine — are formed.

Consequently, in the photolysis of (I) in aprotic solvents in the absence of O_2, the (III) formed in the triplet state in the primary processes enters into the reactions characteristic of triplet aromatic nitrenes [17]: dimerization to derivatives of azobenzene, abstraction of a hydrogen atom from the solvent with the formation of amines. At a concentration of (I) > 10^{-4} M, the abstraction of a hydrogen atom from (I), leading to the formation of polymers [17], becomes substantial.

Photolysis in the Presence of Oxygen. In the course of the irradiation of (I) in the presence of O_2, products absorbing in the visible region of the spectrum are also formed. This absorption reaches the steady-state value and begins to decrease after prolonged irradiation, which is evidence of further photochemical conversions of the primary photolysis products. However, the characteristic time of photochemical conversions of the primary products is an order of magnitude greater than the time of their formation. For the accumulation of the products, photolysis was conducted in small portions, monitoring the absence of further conversions according to the spectra. Chromatographic analysis showed the presence of two main products with R_f 0.51 and 0.28. The first has R_f and absorption spectra (λ_{max} 227, and 376 nm, MeOH; PMR, ppm: 4.29 s, 6.54 d, 6.59 d, 7.99 d, 8.04 d), characteristic of p-nitroaniline (V). The second product is probably p-nitrosoaniline (VI) (peak of the molecular ion m/z 122), which was also confirmed by countersynthesis of (VI) according

TABLE 1. Overall Chemical Yields of p-Nitroaniline (Φ_1) and p-Nitrosoaniline (Φ_2) and Ratio of the Yields Φ_1/Φ_2 in Various Solvents

Solvent	Hexane	3-Methylpentane	3,3-Dimethylpentane	Toluene	Benzene	Acetonitrile	Xe	CO_2
Φ_1/Φ_2 *	2,40	2,80	2,30	0,76	0,63	0,53	1,65	1,44
$\Phi_1 + \Phi_2$, % †	68	77	69	83	80	67	—	—

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*Accuracy of the determination 10%.

†Accuracy of the determination 5%.

to [8, 9] (p-nitrosoaniline, yield 30%, mp 173°C from ether. Found: C 58.99; H 5.09; N 22.79%. Mol. wt. 122. Calculated: C 59.02; H 4.92; N 22.95%. Mol. wt. 122.128). The second product and (VI) have the same values of R_f, mass spectra, PMR spectra (4.6 s, 6.62 d, 6.68 d, 7.76 s), and two UV absorption bands [λ_{max} 270 and 408 nm, $\varepsilon = 7.6 \cdot 10^3$ and $3.7 \cdot 10^4$ liters/(mole·cm), respectively, MeOH].

The overall chemical yields of (V) and (VI) and the ratio of their yields for all solvents (Table 1) coincide within the limits of the experimental accuracy for solutions with the natural content of O_2 and saturated with O_2 at atmospheric pressure. The quantum yield of the formation of (VI) in toluene is 0.43; taking its chemical yield into account, the quantum yield of photolysis of (I) is equal to 0.96.

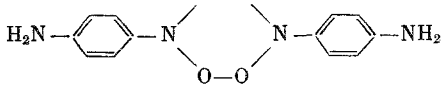
To determine the mechanism of the formation of (V) and (VI), we conducted the photolysis of (I) at 77°K. In glassy solutions of (I), preliminarily saturated with O_2, just as under oxygen-free conditions, (III) in the triplet state is formed and stabilized. Let us note that in the ESR spectrum, in addition to the broad line 6713 Oe, a signal at g = 2.012 was also recorded, evidently belonging to a radical side product.

When irradiated samples are heated to 105°K in toluene with THF or to 98°K in methylcyclohexane, the signal at 6713 Oe and the absorption spectrum characteristic of (III) disappear, and a compound is formed whose spectrum represents a structureless band in the region of 25,000-15,000 cm^{-1}. In the ESR spectrum, in this case no new lines indicating the formation of paramagnetic particles appear. In the absence of O_2, no analogous changes in the absorption spectrum are observed. Consequently, triplet (III) enters into a reaction with O_2 and gives an adduct with characteristic absorption in the visible region of the spectrum [4]. The possibility remains that this adduct may be diamagnetic.

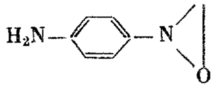
In the course of further heating of the sample at 115°K, the adduct of (III) with O_2 is converted to a compound possessing $\nu_{max} = 29{,}800$ cm^{-1} in methylcyclohexane and ν_{max} 31,400 cm^{-1} in toluene with THF. And only when the matrices are thawed are the stable end products formed — (V) and (VI) — in comparable amounts. The different form of the spectra of the end products of photolysis in the solvents used is due to the different ratio of the chemical yields of (V) and (VI).

Consequently, (V) and (VI) are formed as a result of dark conversions of the primary photochemical product — triplet (III); their common precursor is the adduct of the triplet (III) with O_2.

According to [4], the structure either of a dimer (A) or of a dioxoazirine compound (B) can be ascribed to the intermediate products obtained at 115°K:



A



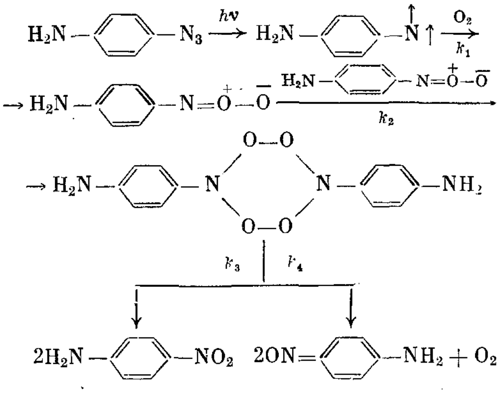
B

Product A can then break down both to two molecules of (V) and to two molecules of (VI) with the release of one molecule of O_2. In the case of the intermediate structure B, the formation of (VI) is possible according to a reaction with a particle capable of taking an O atom. If both intermediate particles (A and B) are realized, then the ratio of the end products should depend on the light intensity. However, a 16-fold change in it does not affect the ratio of the products in hexane, and, consequently, only one intermediate particle is realized. It was noted above that the formation of (VI) from B requires the presence of an im-

TABLE 2. Influence of an Addition of Triethylamine on the Ratio of the Chemical Yields of p-Nitro- and p-Nitrosoaniline

Solvent	Triethylamine concentration, M		
	0	0,01	0,1
Hexane	2,40	0,96	0,79
Toluene	0,76	0,61	0,11

purity capable of accepting an O atom. After thorough purification of the solvents according to the procedures described earlier, the ratio of the products in hexane and toluene remained unchanged. Moreover, comparable amounts of (VI) and (V) are also obtained in liquified CO_2 and Xe. The content of comparable amounts of impurities in all the investigated solvents, including CO_2 and Xe, is rather improbable. Therefore, it can be considered that the intermediate product is a dimer derivative. The complete scheme of conversions can be represented in the form



The ratio of the rate constants k_3/k_4 in this case is equal to the ratio of the yields of (V) and (VI) (see Table 1); the ratio of the products is correlated with the polarity of the matrix. In nonpolar solvents (hydrocarbons, CO_2, Xe) (V) predominates, while in solvents with a high dielectric permeability (CH_3CN) or polarizability (benzene, toluene), (VI) is predominantly formed. Therefore, the formation only of nitrosobenzene in the photolysis of azidobenzene in [6] can be explained by the utilization of a polar solvent.

Whereas the purification of hexane (cp grade) and toluene (analytical grade and cp grade) did not lead to any change in the ratio of the yields of (V) and (VI), the purification of benzene (cp grade) increases the ratio from 0.4 to 0.63, equal to the ratio in chromatographically pure benzene. Moreover, the yield of (VI) can be increased by additions of triethylamine (TEA) (Table 2). In this case the spectral changes observed in the course of annealing of a sample irradiated at 77°K in the presence of 0.1 M TEA differ substantially from those cited previously. The spectrum of the adduct consists of two bands, the ratio between which varies in the course of annealing, which is due to the formation of a complex of the diamagnetic adduct with TEA; moreover, in the course of annealing at 100°K in methylcyclohexane and 105°C in toluene with THF, a compound is already formed, the absorption spectrum of which is similar to the spectrum of (VI). Most likely, (VI) is formed in this case according to the reaction of a diamagnetic adduct with TEA. In the course of annealing at 110°C in methylcyclohexane and 116°K in toluene with THF, in addition to an increase in the absorption in the region of (VI), the absorption characteristic of the dimer product reaches a maximum. When the samples are thawed, the dimer product disappears, giving (V) and (VI), just as before. The change in the spectrum of the end product is evidence of an increase in the yield of (VI). Consequently, we can suggest a second channel of formation of (VI) — the reaction of the adduct with a particle capable of accepting an O atom.

CONCLUSIONS

1. The photolysis of p-azidoaniline in organic aprotic solvents was investigated in the absence of O_2; the main product of photolysis at room temperature is 4,4'-diaminoazobenzene, but when samples irradiated at 77°K are thawed, the main products are 4,4'-diamino-

azobenzene and p-phenylenediamine. The precursor of the end products is p-aminophenylnitrene in the triplet state.

2. In the presence of O_2, the main products of the photolysis of p-azidoaniline in aprotic solvents are p-nitroaniline and p-nitrosoaniline. The quantum and chemical yields of their formation were measured.

3. p-Aminophenylnitrene reacts with O_2 to form an adduct; subsequently, a dimer is obtained, which breaks down to the end products.

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DETERMINATION OF STANDARD ENTHALPIES OF COMPLEXATION OF CALCIUM SALTS WITH 18-CROWN-6 BY MEANS OF SCANNING CALORIMETRY

V. P. Solov'ev, O. A. Raevskii,
and V. E. Zubareva

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It is known that the enthalpy of reaction or the standard enthalpy of formation of condensed substances can be determined by means of scanning calorimetry: The enthalpy of dissolution is determined in any selected solvent, first testing the original reactants and then testing the reaction products in the original solvent; the stoichiometry is taken into account in the calculations [1, 2].

Here we are reporting on the use of this scheme to determine the standard enthalpy of reaction of $CaCl_2$ (s) and $Ca(NO_3)_2$ (s) with 18-crown-6 (I) (s) to form the complexes $CaCl_2 \cdot$ (I) (s) and $Ca(NO_3)_2 \cdot$(I) (s).

EXPERIMENTAL

The crystal hydrate $Ca(NO_3)_2 \cdot 4H_2O$, grade ch.d.a. ("analytically pure"), with a content of principal substance >98.5% by weight, was dehydrated by heating at 445°K for 18-20 h, to constant weight [3], after which it was stored over P_2O_5. The anhydrous $Ca(NO_3)_2$ was charged to a sealed capsule of a DAK-1-1A calorimeter in an atmosphere of dry Ar, or in the muffle furnace at 445-465°K. The crystal hydrate $CaCl_2 \cdot 6H_2O$, grade os.ch. 14-1 ("ultrapure 14-1")

Institute of Physiologically Active Substances, Academy of Sciences of the USSR, Chernogolovka. Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev.
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