Formation of Nitroso Oxides in the Photolysis of Aromatic Azides: Analysis of Products; Reaction Kinetics and Mechanism

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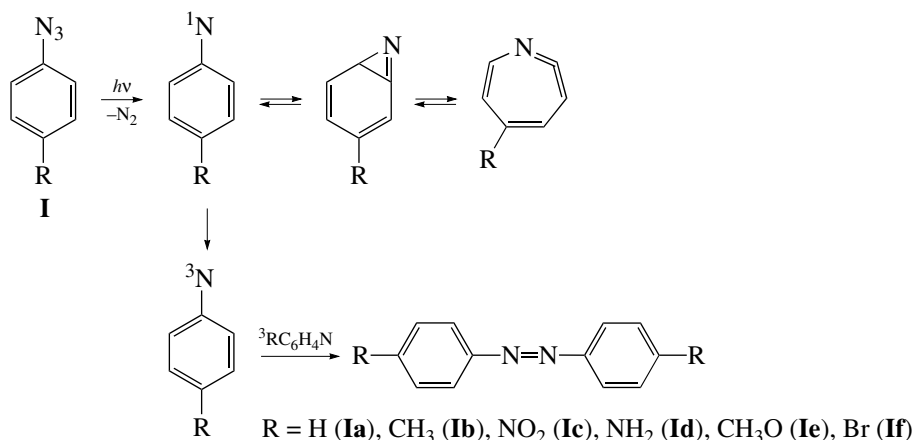*** Bashkortostan State University, Ufa, 450074 Bashkortostan, Russia*
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Abstract—The formation of nitroso oxides (ArNOO) **IIa–IIc** and **IIf** was observed in the flash photolysis of solutions of phenylazide (**Ia**), 4-methylphenylazide (**Ib**), 4-nitrophenylazide (**Ic**), and 4-bromophenylazide (**If**) in acetonitrile in the presence of oxygen, and the optical spectra of these nitroso oxides were obtained. The kinetics of generation (using **IIa** and **IIc** as examples) and decay of nitroso oxides **IIa–IIc** and **IIf** were studied. The activation parameters of the formation of **IIa** by the reaction of triplet phenylnitrene with molecular oxygen ($\log k_{O_2} = (9.6 \pm 0.4) - (18 \pm 2)/2.303RT$ (k_{O_2}, l mol^{-1} s^{-1}; E_a, kJ/mol)) and the unimolecular isomerization of **IIa** into dioxaziridine ($\log k_{iso} = (9.0 \pm 0.8) - (56 \pm 5)/2.303RT$ (k_{iso}, l mol^{-1} s^{-1}; E_a, kJ/mol)) were determined. The kinetics of formation of the molecular products of **Ia** photooxidation were studied using high-performance liquid chromatography. Nitrobenzene was the only stable reaction product (except for tars). A reaction scheme which is consistent with the experimental results was proposed for the photooxidation of **Ia**.

INTRODUCTION

Nitroso oxides ArNOO, which are formed in the reaction of triplet nitrenes ^{3}ArN (azide photodegradation products) with molecular oxygen, are intermediates in the photooxidation of aromatic azides ArN$_3$ [1, 2]. According to published data [3, 4], the mechanism of ArN$_3$ photolysis includes the following main steps (Scheme 1):
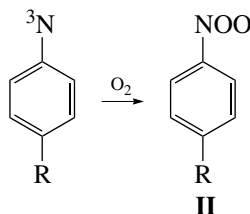

Scheme 1.

Singlet nitrenes **I** undergo reversible isomerization with ring enlargement through the corresponding benzazirines into dehydroazepines [3–6] or intersystem crossing to form triplet nitrenes [5]. Strong electron-acceptor substituents affect the competition of these reaction paths of ^{1}ArN consumption in favor of the latter. Thus, si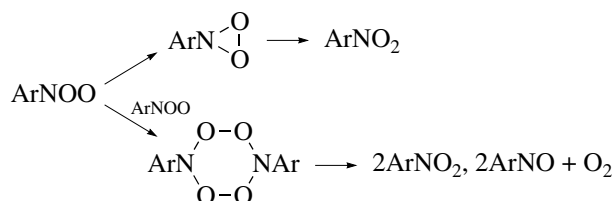nglet 4-nitrophenylnitrene (a photolysis product of **Ic**) was almost completely converted into triplet 4-nitrophenylnitrene [7]. The singlet–triplet (ST) splitting in nitrenes is noticeably greater than that in carbenes. For example, $\Delta E_{ST} = 11$–17 kJ/mol for diphenylcarbene (Ph$_2$C:) [8], whereas $\Delta E_{ST} = 75$ kJ/mol for phenylnitrene (PhN:) [9, 10]; because of this, the S ⟶ T transition in nitrenes is practically irreversible. Triplet

nitrenes undergo further recombination into the corresponding azobenzenes or add $^3O_2$ in aerated solutions to form nitroso oxides (**II**):

R = H (**IIa**), CH₃ (**IIb**), NO₂ (**IIc**), NH₂ (**IId**), CH₃O (**IIe**), Br (**IIf**)

Nitroso oxides were detected for the first time with the use of electronic and EPR spectroscopy in low-temperature vitreous matrices [11]. More recently, they were identified in solutions using flash photolysis [2, 12]. Scarce and discrepant data on the reaction kinetics of nitroso oxides are limited by the rate constants of formation of 1-pyrenylnitroso oxide [13] and formation and decay of compounds **IIb–IId** [12]. According to Brinen and Singh [11], arylnitroso oxides can be consumed in unimolecular reactions to isomerize into dioxaziridine followed by conversion into a nitro compound or in bimolecular reactions with the formation of a dimeric peroxide, which undergoes degradation into either two nitro compound molecules or two nitroso compound molecules and oxygen (Scheme 2):

Scheme 2.

Gritsan and Pritchina [12] found that compound **IId** was consumed in a bimolecular reaction with a near-diffusion rate constant. However, Sawaki and coauthors [14–16], who used a tracer method, found that compounds **IIa**, **IIc**, and **IIe** isomerized into the corresponding nitrobenzenes through dioxaziridine. The photoinduced conversion of nitroso oxides (substituted stilbene derivatives) into dioxaziridines was observed in 2-methyltetrahydrofuran at 77 K [17].

In this work, to obtain additional data on the kinetics and mechanisms of reactions with the participation of nitroso oxides, we studied the kinetics of generation (using **IIa** and **IIc** as examples) and decay of nitroso oxides **IIa–IIc** and **IIf** in acetonitrile solutions using flash photolysis with high-speed spectrophotometric detection. We also studied the kinetics of formation of the molecular products of **Ia** photooxidation using high-performance liquid chromatography (HPLC).

EXPERIMENTAL

Acetonitrile and benzene were purified in accordance with a well-known procedure [18]. Azide **Ia** was synthesized according to Lindsay and Allen [19], whereas azides **Ib**, **Ic**, and **If** were synthesized according to Smith and Boyer [20]. Azides **Ia**, **Ib**, and **If** were distilled in a vacuum; compound **Ic** and benzophenone were recrystallized from ethanol. Nitrobenzene was synthesized in accordance with a published procedure [21] and recrystallized from ethanol ($T_m = 37–38°C$; according to published data, $T_m = 38–39°C$).

The photooxidation products of **Ia** were studied under conditions of continuous photolysis. A DRT-1000 mercury quartz lamp served as a photolytic light source; the radiant energy flux was 95–110 W over the wavelength range 270–380 nm; the distance from a reactor to the light source was 15 cm. Acetonitrile (15 ml) and compound **Ia** ($1.25 \times 10^{-4}–1.0 \times 10^{-2}$ mol/l) were placed in a cylindrical reactor thermostatted at 293 K. Oxygen or air was bubbled through the solution in the course of photolysis with light at $\lambda = 270–380$ nm (UFS-2 light filter). Sampling was performed at regular intervals, and the samples were analyzed by HPLC. The photolysis of nitrobenzene in acetonitrile (1.0×10^{-4} mol/l) was performed under analogous conditions. In the course of the reaction, changes in the UV spectrum of the solution were monitored on a Specord UV–VIS instrument.

The kinetic experiments were performed using a flash photolysis system with spectrophotometric detection; the design of this system was described elsewhere [22]. The reactor was a quartz cell with an optical path length of $l = 10$ cm and an inner diameter of ~1 cm. To prevent azide degradation under exposure to a probe beam, light in the region of azide absorption was attenuated with the use of a BS-4 light filter (transmission region at $\lambda > 300$ nm). The photolysis of arylazide solutions with concentrations of $(0.5–5.0) \times 10^{-4}$ mol/l was performed with filtered light (UFS-2 light filter; transmission region at $\lambda = 270–380$ nm). A BS-7 light filter (transmission region at $\lambda > 350$ nm) was used in benzophenone-photosensitized photolysis.

Chromatographic analyses were performed on a Waters 600E instrument with a Waters 484 detector. Column, μ-Porasil (305 × 4.6 mm) (Waters); mobile phase, ethyl acetate (2–3 vol %)–hexane; flow rate,
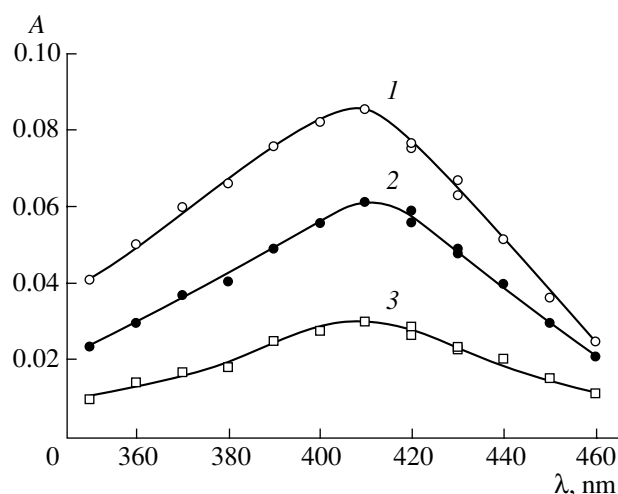
Fig. 1. Optical absorption spectra of compound **IIa** in an acetonitrile solution at 293 K: (*1*) immediately after a pulse, (*2*) 2 s after a pulse, and (*3*) 10 s after.

1–2 ml/min; pressure, 15 MPa; UV detection (280 nm). The retention times of compound **Ia**, nitrosobenzene, and nitrobenzene were 260, 300, and 410 s, respectively.

RESULTS AND DISCUSSION

Identification and Spectroscopic Properties of Arylnitroso Oxides

In the flash photolysis of acetonitrile solutions of compound **Ia** saturated with oxygen or air, optical absorption in the wavelength region 350–460 nm was observed, which disappeared in a matter of seconds. The position of an absorption band maximum (λ_{max} = 410 nm) and the shape of the optical spectrum remained unchanged with time (Fig. 1). This fact suggests that this signal corresponds to a single intermediate. In the flash photolysis of a solution of compound **Ia**, which was purged with argon, this signal was not detected. Taking into account the well-known photolability of **Ia** and the necessity of O_2 for the formation of the observed species, we can reliably attribute the optical absorption detected under conditions of flash photolysis to phenylnitroso oxide **IIa**.

After a light pulse, the absorbance of **IIa** increased in accordance with an exponential law to reach a maximum value in ~100 ms (Fig. 2a, curve *1*); next, it decreased within ~30 s (Fig. 2b). At $\lambda < 420$ nm, the kinetic curves of consumption of compound **IIa** exhibited residual absorbance due to the absorption of stable reaction products. It is likely that products were formed both during a light pulse and after its termination. This makes kinetic measurements difficult to perform over the spectral region at $\lambda < 420$ nm. At $\lambda \geq 420$ nm, the measured absorbance decreased to zero with time; the curves of consumption of compound **IIa** correspond to a first-order rate equation (Fig. 2b).

Intermediate absorbance was also detected in the flash photolysis of solutions of compounds **Ib** and **If**. The spectroscopic pattern observed was qualitatively similar to the above behavior in the flash photolysis of **Ia**; this fact allowed us to correlate optical signals with the absorption of nitroso oxides **IIb** and **IIf**. The kinetic curves of consumption of **IIb** and **IIf** exhibited residual absorbance at $\lambda < 430$ nm (**IIb**) and $\lambda < 410$ nm (**IIf**). The absorption band maxima of compounds **IIb** and **IIf** were at 415 and 420 nm, respectively.

In the flash photolysis of deaerated solutions of compound **Ic**, a substance that absorbs light in the wavelength range 350–460 nm was accumulated during a light-pulse time. Taking into account the aforementioned high probability of the generation of triplet 4-nitrophenylnitrene, we can conclude that this substance is 4,4'-dinitroazobenzene, the recombination product of triplet nitrenes (Scheme 1). This reaction, whose rate constant is equal to 1×10^9 l mol^{-1} s^{-1} [7], competes with the reaction of a triplet nitrene with oxygen. Therefore, as the concentration of O_2 was increased, the yield of azobenzene decreased because the contribution of the latter reaction increased. In the flash photolysis of a solution of **Ic** saturated with oxygen, the reaction of a triplet nitrene with O_2 became predominant, and a signal that corresponds to **IIc** was detected in the wavelength range specified. The intensity of this signal decreased practically to zero with time at $\lambda \geq 380$ nm. The optical spectrum of **IIc** exhibited two absorption maxima with approximately equal intensities at 375 and 420 nm. The consumption of **IIc** occurred in accordance with the first-order rate law.

Kinetics of Formation of Arylnitroso Oxides

The kinetics of ArNOO formation under conditions of the flash photolysis of azides was studied using compounds **IIa** and **IIc** as examples. It was found that the rate of buildup of compound **IIa** is independent of oxygen concentration in solution. This fact suggests that the formation of a triplet nitrene is a rate-limiting step in the generation of **IIa**. The treatment of the kinetic curves of buildup of the absorbance of **IIa** using nonlinear regression analysis in accordance with the equation

$$A = A_\infty(1 - e^{-k_{gr}t}) \qquad (1)$$

with unknown rate constant k_{gr} and limiting absorbance A_∞ gave $k_{gr} = (27.6 \pm 0.6)$ s^{-1} (293 K). Our results are consistent with data published by Gritsan and Pritchina [12], who observed the independence of the rate of formation of **IIb** from [O_2]. A probable reason for this consists in the occurrence of an equilibrium between a singlet nitrene and dehydroazepine (Scheme 1); this equilibrium is strongly shifted toward the latter.

To obtain a triplet nitrene without the intermediate formation of ^{1}PhN, we used benzophenone as a triplet sensitizer for the decomposition of **Ia**. To prevent the
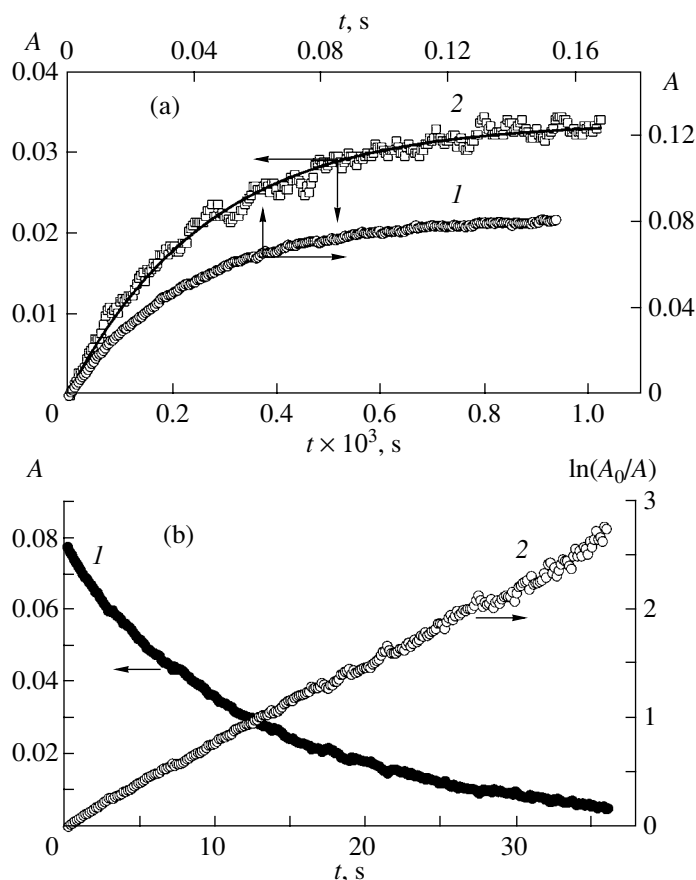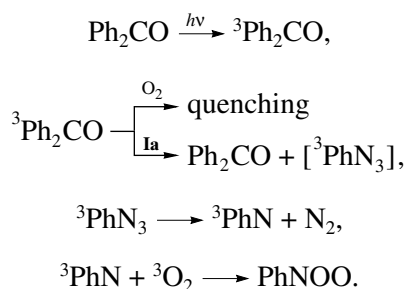
Fig. 2. (a) Kinetic curves of an increase in the absorbance of compound **IIa** in acetonitrile at 293 K measured at a wavelength of 420 nm in air: (*1*) in the absence of a sensitizer; [**Ia**] = 1.25×10^{-4} mol/l; (*2*) initial portion of the kinetic curve in the benzophenone-sensitized flash photolysis of **Ia** and its description with the use of nonlinear regression analysis in accordance with a first-order equation (solid line); [**Ia**] = 4.00×10^{-4} mol/l; [Ph_2CO] = 6.0×10^{-2} mol/l. (b) (*1*) Kinetic curve of decay of the absorbance of **IIa** measured at a wavelength of 420 nm at 293 K and (*2*) its semilogarithmic anamorphosis. Solvent, acetonitrile; [**Ia**] = 1.25×10^{-4} mol/l.

photodegradation of **Ia**, we used a 150-fold amount of benzophenone with respect to the azide ([PhN_3] = 4.0×10^{-4} mol/l and [Ph_2CO] = 6.0×10^{-2} mol/l) and a BS-7 light filter with the transmission region at $\lambda >$ 350 nm. In this case, the reaction scheme of the formation of compound **IIa** is as follows:

$$Ph_2CO \xrightarrow{h\nu} {}^3Ph_2CO,$$

$${}^3Ph_2CO \begin{array}{c} \xrightarrow{O_2} \text{quenching} \\ \xrightarrow{\textbf{Ia}} Ph_2CO + [{}^3PhN_3], \end{array}$$

$${}^3PhN_3 \longrightarrow {}^3PhN + N_2,$$

$${}^3PhN + {}^3O_2 \longrightarrow PhNOO.$$

Nevertheless, we failed to completely prevent singlet nitrene formation: the kinetic curves of buildup of compound **IIa** consisted of two portions, steep (~60%), at which the [O_2] dependence was observed, and gentle, the occurrence of which we cannot explain.

The benzophenone-photosensitized decomposition of compound **Ia** was performed at various oxygen concentrations in solution; these concentrations were var-
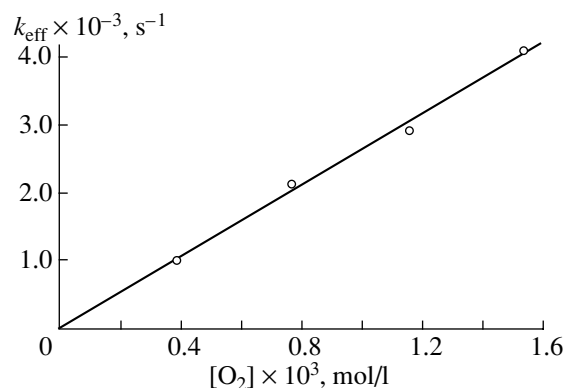

Fig. 3. Dependence of the effective rate constant of buildup of compound **IIa** on the concentration of oxygen at 293 K. Solvent, acetonitrile; [**Ia**] = 4.00×10^{-4} mol/l; [Ph_2CO] = 6.0×10^{-2} mol/l.

Rate constants of the unimolecular decay of arylnitroso oxides in acetonitrile

Arylnitroso oxide	T, K	k_{iso}, s^{-1}
IIa	293	0.10 ± 0.01
	303	0.18 ± 0.01
	314	0.39 ± 0.01
	324	0.82 ± 0.01
	333	1.86 ± 0.08
IIb	295	0.16 ± 0.01
IIc	295	0.092 ± 0.003
IIf	295	0.24 ± 0.02

ied with the use of argon–air gas mixtures. The value of $[O_2]$ was calculated based on published data on the solubility of oxygen in acetonitrile [23]. The oxygen-concentration-dependent steep portion of the kinetic curve of buildup of **IIa** was treated using Eq. (1) (Fig. 2a, curve 2), and the effective rate constant k_{eff} was found. The dependence of k_{eff} on the concentration of oxygen was linear (Fig. 3); the absolute rate constant of the reaction of triplet phenylnitrene with oxygen $k_{O_2} = (2.44 \pm 0.09) \times 10^6$ l mol^{-1} s^{-1} (293 K) was calculated from the slope of this function.

The activation parameters of the reaction ^{3}PhN + O$_2$ were determined over the temperature range 273–313 K: $\log A = 9.6 \pm 0.4$ (l mol^{-1} s^{-1}); $E_a = 18 \pm 2$ kJ/mol. The rate constant is consistent with the rate constants of the reactions of arylnitrenes and oxygen with the formation of compounds **IIb–IId** [12] and 1-pyrenylnitroso oxide [13].

In the flash photolysis of **Ic**, a triplet nitrene was the main primary product [7]; therefore, the concentration of oxygen in solution was responsible for the rate of formation of compound **IIc**. However, it is difficult to plot k_{eff} as a function of $[O_2]$ because the above 4-nitrophenylnitrene recombination, which competes with the test reaction, occurred as the concentration of O$_2$ decreased. Therefore, the value of k_{O_2} was determined as $k_{eff}/[O_2]$ only in a solution saturated with oxygen. Thus, the buildup of **IIc** is characterized by the rate constant $k_{O_2} = (1.31 \pm 0.04) \times 10^6$ l mol^{-1} s^{-1} (295 K), which is consistent with published data for 285 K: $(1.1 \pm 0.1) \times 10^6$ l mol^{-1} s^{-1} (solvent: ethanol) and $(8 \pm 1) \times 10^5$ l mol^{-1} s^{-1} (hexane) [12].

A dramatic difference in reactivity between the interactions of arylnitrenes and aromatic carbenes (their carbo analogs) with oxygen should be noted. Thus, in an acetonitrile or Freon 113 solution at room temperature, the rate constants of formation of diphe-

nylcarbonyl oxide, 4,4'-dimethyldiphenylcarbonyl oxide, and fluorenone oxide (k_{O_2}) are equal to 5.0×10^9, 2.2×10^9, and 1.4×10^9 l mol^{-1} s^{-1}, respectively [24]. It is likely that this reaction occurs practically without an activation energy, and it is limited by the diffusion of reactants to each other. The difference by three orders of magnitude between the values of k_{O_2} for carbenes and nitrenes is a consequence of the activation nature of the interaction of triplet nitrenes with oxygen. Of course, the mechanism of this reaction deserves further investigation.

Kinetics of Arylnitroso Oxide Consumption

As mentioned above, the consumption of all the test arylnitroso oxides occurred in accordance with a first-order rate equation. Nitroso oxides did not react with parent azides because the rate constants, which were determined from the slope of ln$A$ as a function of t, remained unchanged upon varying the concentration of compounds **Ia–Ic** and **If** over the range $(0.5–5.0) \times 10^{-4}$ mol/l. Consequently, the unimolecular consumption of **IIa–IIc** and **IIf** was due to nitroso oxide isomerization into a molecular compound, hypothetically, dioxaziridine. The rate constants of isomerization k_{iso} were determined from absorbance values at different wavelengths within the spectral region in which the accumulation of residual absorbance due to reaction products was not observed (see above). In this region, the rate constant k_{iso} was practically independent of detection wavelength. The table summarizes the values of k_{iso} for the test nitroso oxides. The following reaction activation parameters were determined for **IIa** at 293–333 K: $\log A = 9.0 \pm 0.8$ (l mol^{-1} s^{-1}); $E_a = 56 \pm 5$ kJ/mol.

Note that the difference between the activation energies of isomerization of **IIa** and isomeric phenyldioxaziridine was 53.9 kJ/mol, as calculated by the UB3LYP/6-31G(d) method with the use of the Gaussian program [25] and corrected for 298 K. On the other hand, it is likely that the preexponential factor, which is lower than the usual values for unimolecular reactions, reflects a dramatic increase in the entropy of activation because of the formation of a strained three-membered ring and a contribution from solvation effects, which should be considerable for polar species such as nitroso oxides (according to UB3LYP calculation data, $\mu = 4.7$ D for **IIa**) and their reaction products.

Phenylazide Photooxidation Products

The photooxidative degradation of arylazides was reported in a number of publications; nevertheless, the mechanism of this process is poorly understood. Abramovitch and Challand [26] studied the photooxidation of compound **Ia** in an acetonitrile solution. The reaction was performed to deep degrees of conversion; in this case, nitrobenzene was detected as the main product.
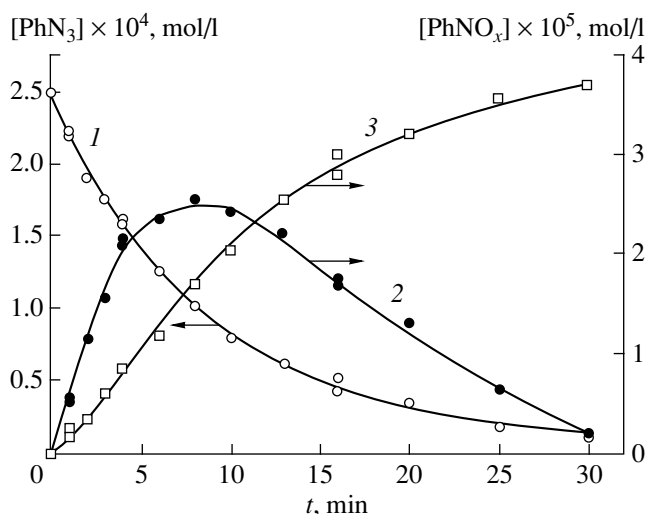
Fig. 4. Kinetic curves of (*1*) consumption of compound **Ia** and formation of (*2*) PhNO and (*3*) PhNO$_2$ obtained in the continuous photolysis of a solution of **Ia** in acetonitrile. Oxygen; T = 293 K; [**Ia**] = 2.50×10^{-4} mol/l.

Fig. 5. The time dependence of the yield of nitrobenzene on consumed **Ia**. Solvent, acetonitrile; T = 293 K. (*1*) [**Ia**] = 1.00×10^{-2} mol/l (bubbling O$_2$); (*2*) [**Ia**] = 1.08×10^{-3} mol/l (bubbling O$_2$); (*3*) [**Ia**] = 2.50×10^{-4} mol/l (bubbling air or O$_2$).

On the other hand, Go and Waddel [27] found that the only stable primary product of the photolysis of **Ia** in acetonitrile saturated with oxygen was nitrosobenzene; next, nitrosobenzene underwent oxidation to nitrobenzene and reacted with the triplet nitrene to form azoxybenzene. In the photooxidation of **Id** in aprotic solvents, 4-nitroaniline and 4-nitrosoaniline were accumulated simultaneously [1, 2, 12]. It is the authors' opinion that these compounds are the decomposition products of a dimeric peroxide formed by the recombination of **IId** (Scheme 2). Note that the formation of tarlike substances in noticeable amounts, probably as a result of the condensation of dehydroazepine, was reported in all of the publications.

Contradictory results obtained by different researchers stimulated us to study the kinetics of formation of the main photooxidation products of compound **Ia** by HPLC. The reaction was performed to >90% conversion of **Ia** with various initial concentrations of the azide. The photolysis was performed in acetonitrile with continuously bubbling air or oxygen at 293 K. We found that nitrosobenzene (PhNO) and nitrobenzene (PhNO$_2$) were the main photooxidation products of **Ia**. We did not observe the formation of azobenzene and azoxybenzene under the conditions of our experiments. An HPLC chromatogram exhibited peaks with long retention times, which probably correspond to dehydroazepine resins.

Figure 4 demonstrates typical kinetic curves of consumption of compound **Ia** and of buildup of PhNO and PhNO$_2$. Note the following most important kinetic regularities of the test process:
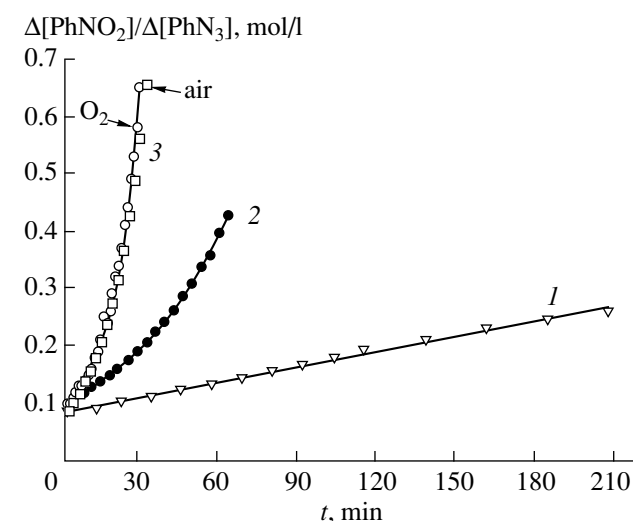
• The azide concentration decreased in accordance with an exponential law.

• The simultaneous formation of PhNO and PhNO$_2$ was observed in the initial period of the reaction.

• Nitrobenzene was practically the only stable product (except for tars) of the photooxidation of compound **Ia**.

• The concentration of nitrobenzene in the reaction mixture initially increased, passed through a maximum, and decreased to zero at the end of the reaction.

• The rates of PhNO formation and consumption weakly depended on the concentration of oxygen in solution.

• The yield of nitrobenzene based on consumed **Ia** increased with conversion. In this case, the yield of nitrobenzene early in the reaction $(\Delta[\text{PhNO}_2]/\Delta[\textbf{Ia}])_{t \to 0}$ was practically independent of the initial azide concentration and equaled ~0.10 (Fig. 5). The total yield of nitrobenzene $(\Delta[\text{PhNO}_2]/\Delta[\textbf{Ia}])_{t \to \infty}$ for [**Ia**] = 2.5×10^{-4} mol/l was ~15%, and it somewhat decreased as the initial azide concentration was increased. The ratio of the rate of buildup of PhNO$_2$ to the rate of consumption of **Ia** $\Delta[\text{PhNO}_2]/\Delta[\textbf{Ia}]$, which was calculated from the slopes of compound **Ia** and PhNO$_2$ concentration curves plotted against time, increased with azide conversion; the lower the initial azide concentration, the greater the degree of this increase (Fig. 5).
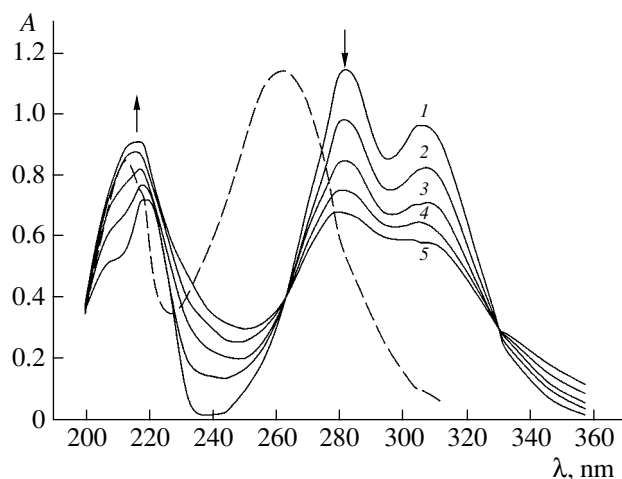
Fig. 6. Changes in the UV spectra of a PhNO solution in acetonitrile in the course of continuous photolysis with bubbling oxygen at 293 K after (*1*) 0, (*2*) 10, (*3*) 20, (*4*) 30, and (*5*) 40 min. [PhNO] = 1.0×10^{-4} mol/l. A dashed line indicates the UV spectrum of a $PhNO_2$ solution in acetonitrile (1.0×10^{-4} mol/l).
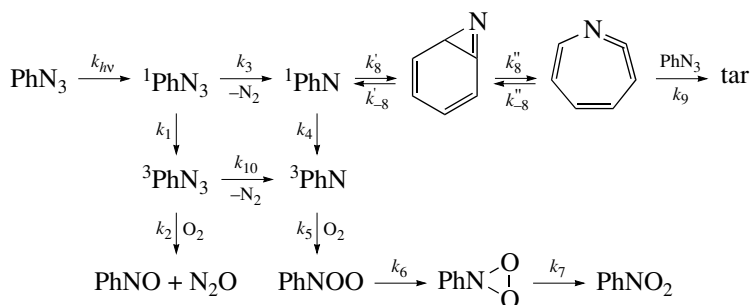
Mechanism of the Photooxidation of Aromatic Azides

The results of analysis of the products of continuous photolysis of compound **Ia** were supplemented with the kinetic data of flash experiments. The unimolecular decay of **IIa** through the intermediate formation of phe-nyldioxaziridine results in nitrobenzene; however, it cannot explain the formation of PhNO. Consequently, these products are formed in parallel reactions. A so-called non-nitrene mechanism [7, 26] can serve as a source of PhNO, when a triplet-excited azide reacts with the oxygen molecule; in this case, PhNO is formed and N_2O is liberated.

A decrease in the concentration of nitrobenzene in the course of the photooxidation of compound **Ia** can be explained by the photolability of this compound. In a control experiment, we found that PhNO underwent photoinduced transformations in the presence of oxygen. However, contrary to a conclusion drawn by Go and Waddel [27], the formation of nitrobenzene was not observed in this case (Fig. 6).

The results of our experiments allowed us to generalize Schemes 1 and 2 by supplementing them with the reactions of excited phenylazide and dehydroazepine. The tar formation process was simulated by the reaction of dehydroazepine with **Ia**. To simplify the reaction scheme, the singlet–triplet conversion of excited PhN_3 and PhN was represented as an irreversible process. This assumption seems reasonable at least for phenylnitrene with consideration for a great difference between the energies of the singlet and triplet states of this species (see above). Thus, the photooxidation mechanism proposed for **Ia** can be represented as the following reaction sequence (Scheme 3):

Scheme 3.

Here, $k_{h\nu}$ is the apparent rate constant of decomposition of compound **Ia**. To simplify the kinetic analysis, we considered two equilibrium steps (between the singlet nitrene and benzazirine and between benzazirine and dehydroazepine) as an overall step (between the singlet nitrene and dehydroazepine). Thus, it should be taken into account that the rate constants k_8 and k_{-8} are the products $k_8' k_8''$ and $k_{-8}' k_{-8}''$, respectively (Scheme 3). The kinetic analysis of the reaction scheme was performed with the use of a quasi-steady-state approximation for the concentrations of electronically excited dehydroazepine, nitroso oxide, and dioxaziridine species. In terms of the proposed reaction scheme, the expression for the rate of nitrobenzene formation has the form

$$\frac{d[PhNO]}{dt} = \frac{k_1}{k_1 + k_3}\frac{k_2[O_2]}{k_2[O_2] + k_{10}}k_{h\nu}[\mathbf{Ia}]$$

$$= (1 - \alpha)(1 - \gamma)k_{h\nu}[\mathbf{Ia}], \qquad (2)$$

where $\alpha = k_3/(k_1 + k_3)$ and $\gamma = k_{10}/(k_2[O_2] + k_{10})$ are the probabilities of singlet-excited and triplet-excited azide degradation, respectively. Equation (2) can explain the weak dependence of the initial rate of nitrobenzene buildup on the concentration of dissolved oxygen if we assume that the product $k_2[O_2]$ is comparable with the rate constant of triplet-excited azide decay k_{10}. In

kinetic experiments, we found that the initial rate of PhNO buildup was equal to 6.6×10^{-8} mol l^{-1} s^{-1} (air); in an atmosphere of oxygen, it was 8.7×10^{-8} mol^{-1} s^{-1} (O$_2$); that is, an increase in the concentration of O$_2$ by a factor of 5 resulted in an increase in the rate by a factor of only 1.32. According to Eq. (2), this corresponds to the rate constant ratio $k_2/k_{10} = 1.5 \times 10^3$ l/mol.

The yield of nitrobenzene based on consumed azide

$$\frac{\Delta[\text{PhNO}]}{\Delta[\textbf{Ia}]} = (1 - \alpha)(1 - \gamma) \qquad (3)$$

can be calculated only early in the reaction because nitrobenzene is labile under conditions of photolysis (see Fig. 4 and the text above). From experimental data, we found that this value is 0.21 or 0.16 in an atmosphere of oxygen or air, respectively.

From a kinetic analysis of Scheme 3, it is easy to derive the following expression for the ratio between the rates of nitrobenzene buildup and **Ia** consumption:

$$\frac{d[\text{PhNO}_2]}{d[\textbf{Ia}]} = \frac{\alpha k_4}{(k_4 + k_8) - (1 - \delta)k_8} + (1 - \alpha)\gamma, \quad (4)$$

where $(1 - \delta) = k_{-8}/(k_{-8} + k_9[\textbf{Ia}])$ is the probability of dehydroazepine conversion into singlet nitrene. At the initial point in time, we can assume that $k_9[\textbf{Ia}]_0 \gg k_{-8}$; whence it follows that

$$\frac{d[\text{PhNO}_2]}{d[\textbf{Ia}]_0} = \left(\frac{\Delta[\text{PhNO}_2]}{\Delta[\textbf{Ia}]}\right)_{t \to 0} = \alpha\beta + (1 - \alpha)\gamma, \quad (5)$$

where $\beta = k_4/(k_4 + k_8)$ is the probability of the singlet–triplet transition for phenylnitrene. Equation (5) explains the independence of the initial yield of PhNO$_2$ on azide concentration, as illustrated in Fig. 5.
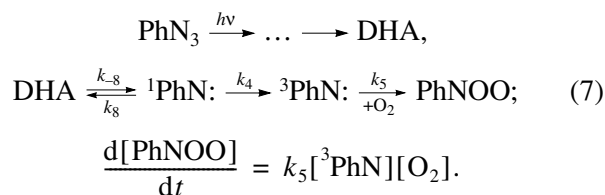
Equation (4) is in qualitative agreement with the experimentally observed ratio between the rates of PhNO$_2$ buildup and **Ia** consumption (Fig. 5). Indeed, an increase in [**Ia**] decreased the value of $(1 - \delta)$; in this case, the denominator in Eq. (4) increased and, consequently, the nitrobenzene yield $d[\text{PhNO}_2]/d[\textbf{Ia}]$ decreased with azide concentration. At complete conversion of **Ia**, the ratio between rates has the form

$$\left(\frac{\Delta[\text{PhNO}_2]}{\Delta[\textbf{Ia}]}\right)_{t \to \infty} = \alpha + (1 - \alpha)\gamma. \qquad (6)$$

Taking into account that $\alpha + (1 - \alpha)\gamma = 1 - (1 - \alpha)(1 - \gamma)$, the limiting yield of nitrobenzene based on consumed azide is 0.84 (air) or 0.79 (O$_2$), which does not contradict experimental results (Fig. 5).

Scheme 3 is consistent with the kinetic results obtained under conditions of flash photolysis of compound **Ia**. Thus, it is evident that $k_{\text{iso}} = k_6$. The independence of the rate of nitroso oxide buildup on the concentration of oxygen under conditions of nonsensitized photolysis of compound **Ia** can be explained as described below. In the flash photolysis of an azide, a high non-steady-state concentration of dehydroazepine

(DHA) was accumulated as a result of fast processes; the consumption of DHA through a reaction sequence resulted in the formation of **IIa**:

$$\text{PhN}_3 \xrightarrow{h\nu} \dots \longrightarrow \text{DHA},$$

$$\text{DHA} \underset{k_8}{\overset{k_{-8}}{\rightleftarrows}} {}^1\text{PhN:} \xrightarrow{k_4} {}^3\text{PhN:} \xrightarrow[+O_2]{k_5} \text{PhNOO}; \qquad (7)$$

$$\frac{d[\text{PhNOO}]}{dt} = k_5[{}^3\text{PhN}][\text{O}_2].$$

It follows from pulse experiments that in the absence of Ph$_2$CO the rate constant of a limiting step is $k_{\text{gr}} = 27.6$ s^{-1}. In the photosensitized photolysis of **Ia**, the rate of formation of compound **IIa** increased by more than two orders of magnitude: $k_5 = k_{\text{O}_2} = 2.44 \times 10^6$ l mol^{-1} s^{-1}; that is, in an atmosphere of oxygen, the effective first-order rate constant is $k_5[\text{O}_2] = 3.76 \times 10^3$ s^{-1}. Consequently, under conditions of the flash photolysis of compound **Ia**, the quasi-steady-state principle can be applied to the concentrations of singlet and triplet nitrenes. Then, for the rate of nitroso oxide buildup, we obtain

$$\frac{d[\text{PhNOO}]}{dt} = \frac{k_4 k_{-8}[\text{DHA}]}{k_4 + k_8} = \beta k_{-8}[\text{DHA}]. \qquad (8)$$

Consequently, the rate of buildup of compound **IIa** is limited by the rate of consumption of dehydroazepine, and the experimentally measured value is $k_{\text{gr}} = \beta k_{-8}$.

REFERENCES

1. Pritchina, E.A., Gritsan, N.P., and Bazhin, N.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, no. 8, p. 1749.
2. Pritchina, E.A. and Gritsan, N.P., *Kinet. Katal.*, 1987, vol. 28, no. 5, p. 1044.
3. Leyva, E., Platz, M.S., Persy, G., and Wirz, J., *J. Am. Chem. Soc.*, 1986, vol. 108, no. 13, p. 3783.
4. Borden, W.T., Gritsan, N.P., Hadad, C.M., Karney, W.L., Kemnitz, C.R., and Platz, M.S., *Acc. Chem. Res.*, 2000, vol. 33, p. 765.
5. Schrock, A.K. and Schuster, G.B., *J. Am. Chem. Soc.*, 1984, vol. 106, no. 18, p. 5228.
6. Chapman, O.L. and Le Roux, J.-P., *J. Am. Chem. Soc.*, 1978, vol. 100, no. 1, p. 282.
7. Liang, T.-Y. and Schuster, G.B., *J. Am. Chem. Soc.*, 1987, vol. 109, no. 25, p. 7803.
8. Eisenthal, K.B., Turro, N.J., Aikawa, M., Butcher, J.A., Jr., Du Puy, C., Hefferon, G., Hetherington, W., Korenowski, G.M., and McAuliffe, M.J., *J. Am. Chem. Soc.*, 1980, vol. 102, p. 6563.

9. Travers, M.J., Cowles, D.C., Clifford, E.P., and Ellison, G.B., *J. Am. Chem. Soc.*, 1992, vol. 114, no. 22, p. 8699.

10. McDonnald, R.N. and Davidson, S.J., *J. Am. Chem. Soc.*, 1993, vol. 115, no. 23, p. 10857.

11. Brinen, J.S. and Singh, B., *J. Am. Chem. Soc.*, 1971, vol. 93, no. 24, p. 6623.

12. Gritsan, N.P. and Pritchina, E.A., *J. Inf. Rec. Mater.*, 1989, vol. 17, nos. 5–6, p. 391.

13. Yamaoka, T., Kashiwagi, H., and Nagakura, S., *Bull. Chem. Soc. Jpn.*, 1972, vol. 45, no. 2, p. 361.

14. Sawaki, Y., Ishikawa, S., and Iwamura, H., *J. Am. Chem. Soc.*, 1987, vol. 109, no. 2, p. 584.

15. Ishikawa, S., Tsuji, S., and Sawaki, Y., *J. Am. Chem. Soc.*, 1991, vol. 113, no. 11, p. 4282.

16. Ishikawa, S., Nojima, T., and Sawaki, S., *J. Chem. Soc., Perkin Trans. 2*, 1996, p. 127.

17. Harder, T., Wessig, P., Bendig, J., and Stosser, R., *J. Am. Chem. Soc.*, 1999, vol. 121, no. 28, p. 6580.

18. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Techniques of Organic Chemistry. Vol. 7. Organic Solvents. Physical Properties and Methods of Purification*, New York: Wiley, 1955.

19. Lindsay, R.O. and Allen, G.F.H., *Org. Synth.*, 1955, vol. 3, p. 710.

20. Smith, P.A.S. and Boyer, J.H., *Org. Synth*, 1963, vol. 4, p. 75.

21. *Sintezy organicheskikh preparatov* (Syntheses of Organic Preparations), Kazanskii, B.A., Ed., Moscow: Inostrannaya Literatura, 1952, no. 3, p. 354.

22. Maslennikov, S.I., Nikolaev, A.I., and Komissarov, V.D., *Kinet. Katal.*, 1979, vol. 20, p. 326.

23. Casal, H.L., Sugamori, S.E., and Scaiano, J.C., *J. Am. Chem. Soc.*, 1984, vol. 106, no. 24, p. 7623.

24. Scaiano, J.C., McGimpsey, W.G., and Casal, H.L., *J. Org. Chem.*, 1989, vol. 54, no. 7, p. 1612.

25. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J., Daniels, M.A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., and Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B.G., Chem, W., Wong, M.W., Andres, J.L., Head-Gordon, M., Replogle, E.S., and Pople, J.A., *Gaussian 98* (Revision A.7), Pittsburgh: Gaussian, 1998.

26. Abramovitch, R.A. and Challand, S.R., *J. Chem. Soc., Chem. Commun.*, 1972, no. 16, p. 964.

27. Go, C.L. and Waddel, W.H., *J. Org. Chem.*, 1983, vol. 48, no. 17, p. 2897.