

para-Substituent Effect on the Decay Kinetics of the Isomeric Forms of Aromatic Nitroso Oxides

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Abstract—Flash photolysis of aromatic azides 4-R-C₆H₄N₃ (where R = Ph, OPh, CH₂Ph) in aerated acetonitrile solutions led to the intermediate formation of *cis* and *trans* isomers of the corresponding aryl nitroso oxides, which then presumably transformed via the aromatic ring opening into R-substituted unsaturated nitrile oxides. The electronic spectra of the *cis* and *trans* isomers of 4-R-C₆H₄NOO were recorded; the effective rate constants of the monomolecular decay of the isomers were determined, and the activation parameters of the rate constants were found. The rate constants k_{trans} are significantly lower than k_{cis} , slightly varying in the series of nitroso oxides in the range 0.15–0.22 s⁻¹ (295 K). The rate constants k_{cis} for phenyl- (2.5 s⁻¹) and benzyl- (2.8 s⁻¹) substituted aryl nitroso oxides coincide within the experimental error, whereas the phenoxy substituent leads to an increase in k_{cis} by a factor of ~1.5 (4.3 s⁻¹). The decay of 4-R-C₆H₄NOO is represented by a system of three elementary reactions, including reversible isomerization of the *cis* and *trans* isomers and *ortho*-cyclization of *cis*-nitroso oxides into the corresponding nitrile oxide. Solving the system of differential equations describing the decay kinetics of 4-R-C₆H₄NOO led to an analytical time dependence of optical density of the reaction mixture, which coincides with the empirical dependence found earlier. This made it possible to reveal the physical meaning of the effective rate constants and calculate the elementary rate constants of the decay of aromatic nitroso oxides. The DFT calculations of activation barriers for *cis*-*trans* isomerization and irreversible *ortho*-cyclization of *cis*-4-R-C₆H₄NOO are in good agreement with experiment.

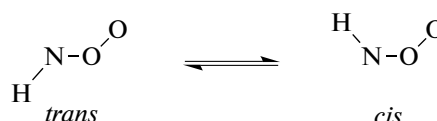
Keywords: flash photolysis, aromatic nitroso oxides, reactivity, *cis*-*trans* isomerism, *ortho*-cyclization, DFT calculation

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INTRODUCTION

Nitroso oxides, labile species of the general formula RNOO from the class of 1,3-dipolar peroxide species X-O-O, are intermediates in the thermal and photochemical reactions involving triplet nitrenes and occurring in the presence of molecular oxygen. The unique properties of nitroso oxides have been studied in recent years and were considered in reviews devoted to organic azides and nitrogen- and oxygen-containing heterocyclic compounds [1–5]. The structure, spectral properties, generation methods, reactivity, and mechanisms of various transformations of aromatic nitroso oxides ArNOO were considered in detail in [6–13].

It was found that simple nitroso oxide HNOO has a planar structure and exists in the form of two stable stereoisomers, *trans* and *cis* [14]:



The electronic structure of HNOO in the ground state is characterized by a three-center 4 π electron system. Additional π bonding leads to an increase in the N–O and O–O bond order and a decrease in the interatomic distances by ~0.15 Å compared to those of the single bonds [15]. In the isomers of HNOO, the ratio of the bond lengths of the nitroso oxide fragment is inverted: in the *trans* isomer, $r(\text{NO}) > r(\text{OO})$, while for the *cis* form, the ratio is inverted because of the anomeric stabilizing interaction $n_{\text{N}} \rightarrow \sigma_{\text{OO}}^*$, which is possible only in the *cis* isomer. For the same reason, the *cis* form of HNOO is thermodynamically more stable than the *trans* form by 8.1–10.9 kJ/mol [16].

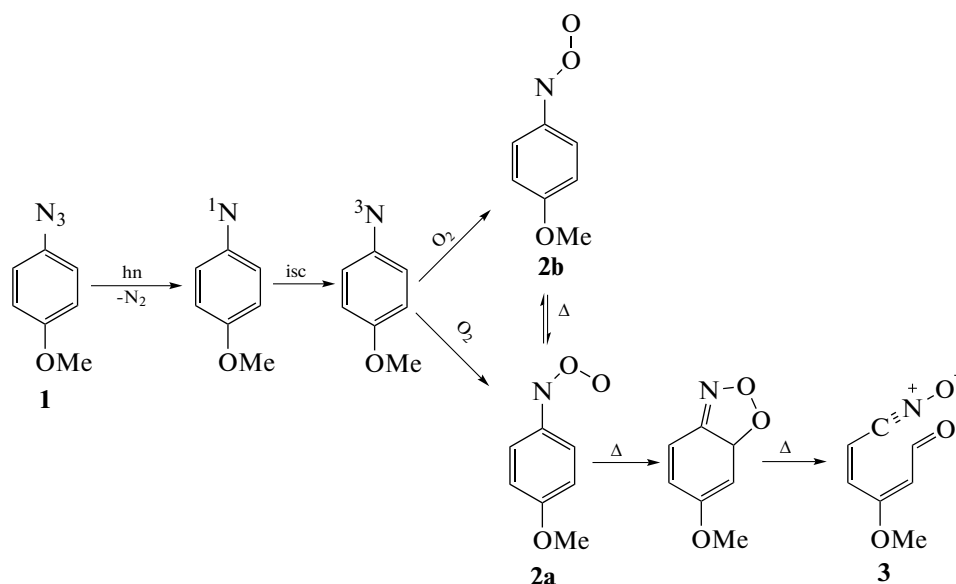
The presence of an aromatic substituent in ArNOO conjugated with the 4 π electron nitroso oxide group significantly stabilizes the latter. Like the simplest

Abbreviations and notation: PES, potential energy surface; HPLC, high-performance liquid chromatography.

nitroso oxide, aryl nitroso oxides also exist in two planar (*cis* and *trans*) conformations, which are close in energy. The *cis* and *trans* states of ArNOO are separated by a significant conformation barrier [17] due to the partial π bonding between the N and O atoms. The relatively low rate of the conformational *cis*–*trans* transition explains the experimental fact, according to which *cis*- and *trans*-ArNOO behave as kinetically independent species that differ in the chemical nature and reactivity. According to theoretical estimates [18], the optical absorption spectrum of HNOO is characterized by a maximum at a wavelength of ~ 260 nm. The formation of a common π electron system markedly shifts the absorption band in the electronic spectra of aromatic nitroso oxides to the long-wave region. The high polarity and dynamicity of the π electron system of aromatic nitroso oxides explains the solvent effect on the distribution of electron density: it was shown [19] that the density increases on the nitroso oxide fragment and the dipole moment of the *cis*–*trans* isomers of the 4-R–C₆H₄NOO series increases with the dielectric permittivity in the series gas phase–*n*-heptane–benzene–acetonitrile.

As nitroso oxides are short-lived intermediates, they were detected for the first time only in 1971 using matrix isolation combined with spectral methods [20]. Today, another method is successfully used at our laboratory to study the isomeric forms of these labile species, namely, flash photolysis with time-resolved spectrophotometry. The use of this method enabled us to identify isomers for a number of aryl nitroso oxides in

media of different polarities at room temperature and higher temperatures. The decay of ArNOO, in contrast to that of related aryl carbonyl oxides Ar₂COO, occurs according to the first-order kinetic law [8] even when there is no substrate of oxidation. The observed kinetic law of the decay of ArNOO was explained using photo-oxidation of 4-methoxyphenyl azide **1** in an acetonitrile solution as an example [9]. It was proved that a nontrivial intramolecular reaction occurs [21], in which the terminal oxygen atom of the *cis* form of nitroso oxide **2a** is coordinated at the *ortho*-carbon atom of the aromatic ring (Scheme 1), forming bicyclic dioxazole. Whether this compound is a stable structure or a transition state is currently unknown. There is no information on the spectral identification of dioxazole, and theoretical estimates give ambiguous results: calculations by the G2MP2B3 method indicate the presence of an activation barrier with a height of 15 kJ/mol for dioxazole decomposition [22], while no minimum corresponding to dioxazole was found on the potential energy surface (PES) of the reaction system when modeling in the M06L/6-311 + G(*d,p*) approximation [23]. In any case, the opening of the metastable dioxazole ring at the C–C and O–O bonds leads to nitrile oxide **3**. Obviously, only the *cis* isomer of nitroso oxide can undergo *ortho*-cyclization. Nevertheless, the authors of [10] showed that both isomers of nitroso oxide **2** are converted into product **3**; i.e., the main channel of the decay of **2b** is its *trans*–*cis* isomerization to **2a**:

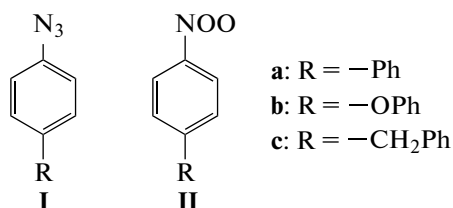


Scheme 1. Mechanism of photo-oxidation of aromatic azides.

The stability of the resulting nitrile oxide **3** changes depending on the electronic properties of the R substituent in the aromatic ring of the starting nitroso oxide. The relatively stable nitrile oxide (R = OMe)

was identified directly by spectrometry [10]. In other cases, the intermediate formation of **3** was recorded according to the stable products of its subsequent intramolecular transformations [12, 23] and (3 + 2)

cycloaddition to the acetonitrile solvent [13]. The driving force of these transformations is the presence of a reaction site—a multiple bond or a lone electron pair at which the electrophilic attack of nitrile oxide occurs with the formation of heterocyclic oximes [23], benzisoxazoles [12], and oxadiazoles [13]. The aromatic substituent in nitroso oxide also represents a potential reaction site for an attack by nitrile oxide, but this possibility has not yet been studied. For this reason, the objects of study here were azides **Ia–Ic** as their photo-oxidation should lead to nitroso oxides **IIa–IIc**, whose structure is of interest to us. However, the reactivity of **IIa–IIc** in *ortho*-cyclization has not been studied. The effect of the properties and position of the R substituent in the benzene ring on the activation barrier ΔH^\ddagger of the intramolecular *ortho*-cyclization of aromatic nitroso oxides was systematically studied theoretically in [21, 24]. As is known, the presence of a substituent in the *ortho* position significantly affects the activation enthalpy of *ortho*-cyclization [24], whereas the role of the *para* substituent is not so obvious [21]. Therefore, here we studied the effect of the substituent in the *para* position on the spectral characteristics of the isomeric forms of aromatic nitroso oxides 4-R-C₆H₄NOO (**IIa–IIc**) and on their kinetic behavior and thermodynamic parameters using flash photolysis of aryl azides 4-R-C₆H₄N₃ (where R = -Ph, -OPh, -CH₂Ph) (**Ia–Ic**) in acetonitrile solutions. The results were compared with the corresponding parameters for other previously studied aromatic nitroso oxides.



EXPERIMENTAL

Acetonitrile (Kriokhrom) for high-performance liquid chromatography (HPLC) was used without preliminary purification. Aryl azides were synthesized according to [25].

The kinetic studies were performed on a flash photolysis unit of known design ENREF-7 [26]. The photolytic source was an IFP 5000-2 lamp (RadioTekhIndustriya, Russia); the maximum pulse energy was 400 J at $U = 5$ kV and $C = 32$ μF ; $\sim 90\%$ of light energy is emitted in 50 μs . The spectrophotometric part of the unit consisted of a probing source of continuous radiation—a DKSSh-150 xenon lamp (Zapadpribor, Russia) with a system of quartz lenses and diaphragms for forming a probing beam; an MDR-4 monochromator (TD Labor, Russia); an FEU-97 photomultiplier (Zapadpribor, Russia); and an S9-8 storage oscilloscope (Kalibr plant, Minsk, Belarus). This unit also

had a device for computer processing of the pulse signal. The signal from the photomultiplier is amplified after preliminary compensation of the DC component and fed to the input of the digital oscilloscope operating in a standby mode. The oscilloscope allows storage of a signal (2048 points) with a minimum time resolution of 50 ns and voltage resolution of 256 levels. The signal was digitized via the GPIB interface (IEEE-488, GPIB). The kinetic curves were processed by nonlinear regression analysis. The error in determining the rate constants was no more than 10%. The reactor was a thermostatted quartz cell with an optical length $l = 10$ cm and inner diameter of ~ 1 cm. The optical spectra of the *para*-substituted phenyl azides **Ia–Ic** studied by us have some features that are similar to those of the spectra of other phenyl azides [27]: the main maximum at 250–260 nm ($\log \epsilon \geq 4$) and a wide shoulder at 280–300 nm ($\log \epsilon \geq 3$), which attenuates near ~ 360 –380 nm. Flash photolysis of aryl azide solutions in acetonitrile was performed with filtered light (UFS-2 light filter, transmission range $\lambda = 270$ –380 nm). The initial concentration of azides was $(1\text{--}2) \times 10^{-4}$ M. To reduce the rate of decomposition of azides under the action of the probing beam, the region of their absorption was cut out with a CC-15 light filter, transmitting light in the wavelength range 300–520 nm, and the probing lamp was covered with a special shutter when preparing the measurement. It was shown by idle experiments that at the indicated concentrations of ArN₃, the decomposition of azide is insignificant within the time of experiment (a few seconds) and does not introduce errors in the results. The activation parameters of the reaction were determined in the temperature range 277–333 K.

All DFT calculations were performed using the M06L density functional [28] and the 6-311 + G(*d,p*) split-valence triple zeta basis set [29, 30]. It was shown [17] that this level of theory adequately reproduces the geometrical structure of aromatic nitroso oxides, their equilibrium and nonequilibrium energy parameters, and the vibrational spectra of ArNOO. The quantum chemical calculations were performed on the cluster supercomputer of the Ufa Institute of Chemistry, Ural Federal Research Center, Russian Academy of Sciences, using the Gaussian 09, Revision C.1 software package [31].

RESULTS AND DISCUSSION

Flash photolysis of the acetonitrile solutions of azides **Ia–Ic** in the presence of atmospheric oxygen produces the *cis* and *trans* isomers of the corresponding nitroso oxides **IIa–IIc**, whose optical absorption spectra are recorded in the wavelength range 380–500 nm. The observed signal decreases to some constant value within a few seconds (Fig. 1). In the range of spectral wavelengths in which light is absorbed by both isomers, the kinetic curves of the decrease in optical density include the fast and slow sections (curve 1, Fig. 1):

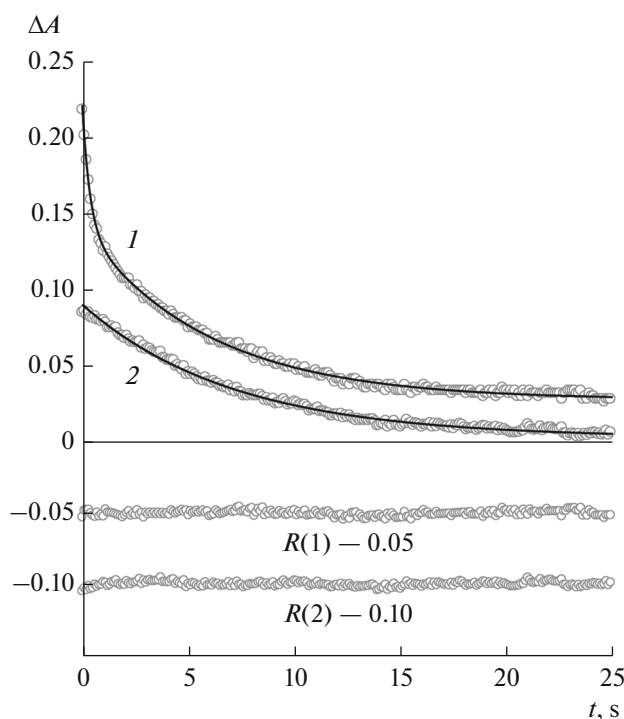


Fig. 1. Typical kinetic curves of the decrease in the differential optical density of the solution of **Ic** ($[Ic]_0 = 2 \times 10^{-4}$ M) after irradiation with light from a flash lamp, recorded at wavelengths of (1) 380 and (2) 460 nm and their approximation (solid lines) by Eqs. (1) and (2), respectively; $T = 295$ K, acetonitrile. Below are the deviations of the approximating function from the experimental values of the optical density R for both kinetic curves.

they correspond to the decay of both forms of ArNOO, which differ in reactivity, and are well described by the five-parameter biexponential equation (1):

$$\Delta A = A_\infty + A_0^{\text{cis}} e^{-k_{\text{cis}} t} + A_0^{\text{trans}} e^{-k_{\text{trans}} t}, \quad (1)$$

where k_{cis} and k_{trans} are the effective rate constants of the monomolecular decay of *cis*- and *trans*-nitroso oxide, respectively; A_∞ is the optical density at the end of the reaction including the formation of reaction products. In the long-wave region of the given spectral range, the kinetic curves consist only of the slow component of Eq. (1) (curve 2, Fig. 1). In this region, the optical absorption of the *cis* isomer is negligible. Thus, the kinetic curves correspond to the decay of only the *trans* isomer and are well described by the first-order kinetic equation:

$$\Delta A - A_\infty = A_0^{\text{trans}} e^{-k_{\text{trans}} t}. \quad (2)$$

The electronic absorption spectra of isomers **IIa–IIc** (Fig. 2) were determined from the calculated $A_0(\lambda)$ values provided that the generation of ArNOO and tracing the optical density at all wavelengths are performed under identical conditions (azide concentration, light pulse energy). The shape of the optical

spectra of **IIa–IIc** and the position of the absorption maxima correspond to the previously established tendencies for other aryl nitroso oxides [8] and to the theoretical calculations [12], according to which the absorption spectra of the *trans* isomer of nitroso oxides are shifted to the long-wave region compared to the spectra of the *cis* isomer. The λ_{max} values for **IIa–IIc** are presented in Table 1, which also contains the data of [8] on the absorption maxima of the isomer forms of phenyl nitroso oxide (**IIId**), 4-methyl- (**IIe**), and 4-methoxyphenyl nitroso oxide (**IIIf**) for comparison. In the series $-\text{H} < -\text{Me} < -\text{Ph}$, a bathochromic shift of the absorption maxima of the *cis* isomers of ArNOO on passing from unsubstituted phenyl nitroso oxide **IIId** to **IIa** is observed. For the *trans* isomers, the bathochromic shift of λ_{max} is even more pronounced. The observed order is appropriate within the framework of color theory: the energy of the electronic $\pi \rightarrow \pi^*$ transition responsible for the absorption band of aryl nitroso oxides in the visible region of the spectrum decreases when the conjugation region in **IIa** increases. The violation of conjugation due to the bridging methylene group $-\text{CH}_2-\text{Ph}$ in nitroso oxide **IIc** leads to a reverse shift of the absorption maximum to a value close to λ_{max} for methyl-substituted ArNOO **IIe**. The oxygen bridge ($-\text{O}-\text{Ph}$) in **IIb** also breaks the conjugation between the two benzene rings located in the perpendicular planes (M06L calculation). However, due to the lone electron pairs, the oxygen atom donates electron density to the π system of aromatic nitroso oxide. The strong donor effect of the $-\text{OPh}$ and $-\text{OMe}$ substituents causes a significant bathochromic shift by 40–50 nm of the absorption maxima of *cis* isomers **IIb** and **IIIf** and by 50–55 nm for the *trans* isomers compared to simple aryl nitroso oxide **IIId**.

It is noteworthy that the ratio $A_0^{\text{trans}}/A_0^{\text{cis}}$ in the absorption maxima of **IIa–IIc** markedly changes depending on the nature of the *para*-substituent (Fig. 2). A similar tendency was observed for nitroso oxides **IIId–IIIf** in [8]. For unsubstituted nitroso oxide and ArNOO with C-centered substituents, this ratio is large (~ 3 – 5). In the optical spectra of **IIb** and **IIIf**, A_0^{cis} is $\sim 80\%$ of A_0^{trans} . The $A_0^{\text{trans}}/A_0^{\text{cis}}$ ratio is evidently affected by the initial concentrations of the *cis*- and *trans*- isomers of ArNOO generated during the photolysis of azides and by the extinction coefficients of the isomers. It is also necessary to take into account the complex kinetic scheme of the decay of nitroso oxides (Scheme 1), according to which the simultaneous occurrence of reversible *cis*–*trans* isomerization and irreversible *ortho*-cyclization can have a significant effect on the calculated values of the pre-exponential terms in Eq. (1). The nature of the observed effect is currently studied in our laboratory.

The effective rate constants for the decay of nitroso oxide isomers **IIa–IIc**, determined using Eqs. (1) and

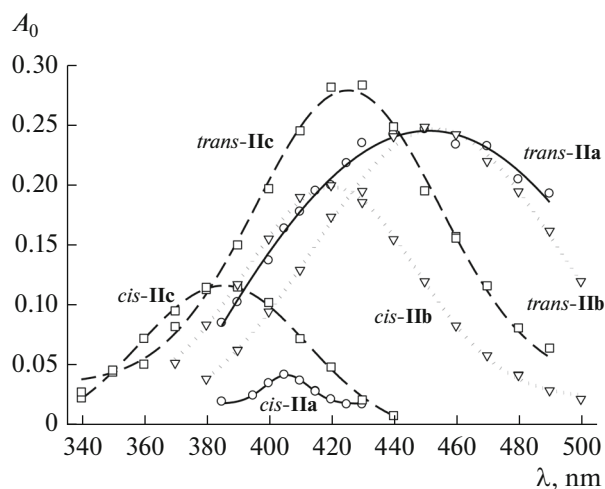


Fig. 2. Optical absorption spectra of the *cis* and *trans* forms of nitroso oxides.

(2) and presented in Table 1, demonstrate tendencies similar to those previously found for **II**d–**II**f and some other aryl nitroso oxides. The rate constants k_{trans} are approximately an order of magnitude lower than k_{cis} , change slightly in the series of nitroso oxides under study, and lie in the range 0.15–0.22 s⁻¹ (295 K). The rate constants k_{cis} for **II**a and **II**c coincide within the experimental error, and the phenoxy substituent leads to an increase in k_{cis} by a factor of ~1.5–2. Table 1 also gives the results for the temperature dependences of the rate constants of the decay of *cis* and *trans* conformers **II**a–**II**c and the literature data for **II**d and **II**f. It can be seen that the activation energies of the decay of both *cis* and *trans* isomers change in the same range of values, 60–70 kJ/mol, and the above-mentioned difference in the reactivity of the isomers is determined primarily by the value of the pre-exponential factor in the Arrhenius equation. It is interesting to note that for both isomers of aryl nitroso oxides, the

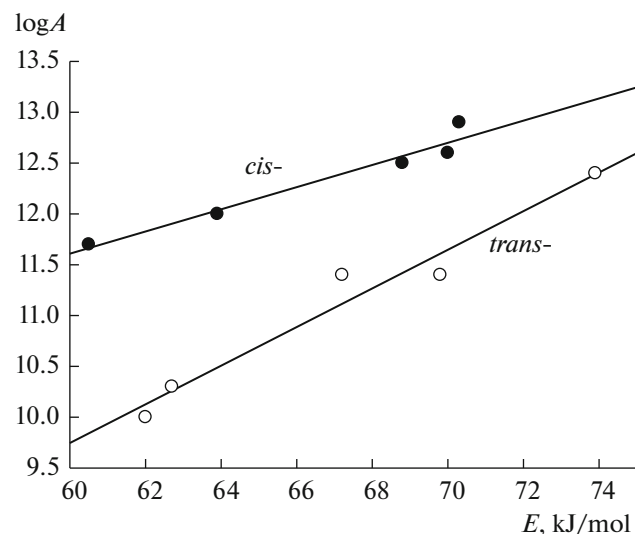


Fig. 3. Compensating effect in the decay reactions of the *cis* and *trans* isomers of aromatic nitroso oxides.

dependence between $\log A$ and the activation energies is close to linear (the correlation coefficient is 0.98 in both cases) (Fig. 3). The compensation effect is associated with the fact that the *trans* isomer decays in the same way for all nitroso oxides under study; i.e., it turns into the *cis* isomer as a result of the conformational rotation at the N–O bond. Similarly, all *cis* isomers **II**a–**II**f undergo irreversible transformation into the corresponding nitrile oxide according to Scheme 1.

Indeed, recently [32], the mechanism of monomolecular decay of *para*-substituted aryl nitroso oxides was shown to be general using photo-oxidation of unsubstituted phenyl azide and its *para*-substituted analogs with electron-donating (MeO) and electron-accepting (Cl, Br) substituents as an example. Along with the main products of conversion of ArNOO—nitrile oxides or the products of their further transformation, relatively small amounts of nitro (ArNO₂) and

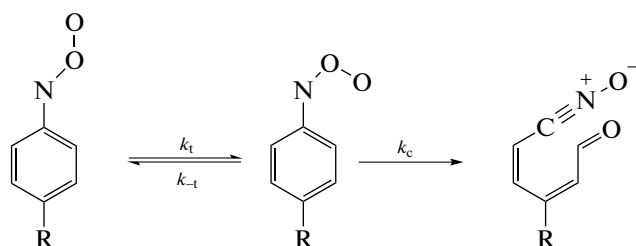
Table 1. Absorption maxima (λ_{max}), effective rate constants (k), and activation parameters ($\log A$, E_{act} , $T = 277$ – 333 K) of the decay of the isomer forms of *para*-substituted phenyl nitroso oxides in acetonitrile

Parameters	Isomer form	Group					
		–Ph	–OPh	–CH ₂ Ph	–H [8]	–Me [8]	–OMe [8]
λ_{max} , nm	<i>cis</i>	405	420	385	380	390	430
	<i>trans</i>	450	455	425	405	425	460
k , s ⁻¹ (295 K)	<i>cis</i>	2.5 ± 0.3	4.3 ± 0.4	2.78 ± 0.06	1.19 ± 0.06	2.25 ± 0.06	11.3 ± 0.2
	<i>trans</i>	0.19 ± 0.02	0.22 ± 0.02	0.15 ± 0.02	0.10 ± 0.01	0.17 ± 0.01	0.37 ± 0.02
$\log A$, (s ⁻¹)	<i>cis</i>	12.9 ± 0.2	12.0 ± 0.1	12.5 ± 0.1	12.6 ± 0.2	–	11.7 ± 0.1
	<i>trans</i>	10.3 ± 0.2	12.4 ± 0.1	11.4 ± 0.2	10.0 ± 0.3	–	11.4 ± 0.2
E_{act} , kJ/mol	<i>cis</i>	70 ± 1	64 ± 1	69 ± 1	70 ± 1	–	60.5 ± 0.3
	<i>trans</i>	63 ± 1	74 ± 1	70 ± 2	62 ± 2	–	67.2 ± 0.9

Table 2. Rate constants of decay (k , s^{-1} , 295 K), activation parameters ($\log A$, s^{-1} ; E , kJ/mol) and M06L/6-311 + G(d,p) activation enthalpies (ΔH^\ddagger , kJ/mol) of the elementary stages of the decay of aromatic nitroso oxides

ArNOO	k_t	$\log A_t$	E_t	ΔH_t^\ddagger	k_{-t}	$\log A_{-t}$	E_{-t}	ΔH_{-t}^\ddagger	k_c	$\log A_c$	E_c	ΔH_c^\ddagger
IIa	0.21	10.2	62.2	68.4	0.20	10.3	62.6	68.9	2.23	12.8	70.5	77.7
IIb	0.22	12.4	73.9	69.6	0.04	12.2	76.9	72.6	4.24	11.9	63.5	74.1
IIc	0.15	11.4	69.9	67.7	0.07	11.2	70.4	68.2	2.71	12.5	68.8	74.4
IId	0.12	9.7	60.4	67.9	0.17	9.8	60.1	67.5	1.00	12.6	70.9	75.9
IIe	0.19	—	—	68.0	0.18	—	—	68.9	2.05	—	—	76.0
IIIf	0.37	11.4	67.3	70.0	0.13	11.6	70.8	73.5	11.16	11.7	60.3	75.2

nitroso compounds (ArNO) are usually recorded in the reaction mixture [12, 13, 23, 32]. We attribute their formation to the photo-induced side reactions of aryl nitroso oxides. Kinetically these reactions can manifest themselves in slightly increased observed rate constants k_{cis} and k_{trans} , and can be neglected within the experimental error. Thus, the formal kinetic scheme of the decay of aromatic nitroso oxides **IIa–IIIf** is reduced to three stages with elementary rate constants k_t , k_{-t} , and k_c (Scheme 2):

**Scheme 2.** Kinetic scheme of the decay of aromatic nitroso oxides.

As all the reactions are monomolecular transformations, for the system of differential equations corresponding to Scheme 2, there is an analytical solution that has the form of a weighted sum of exponentials [17]. Passing from concentrations to optical densities, it is easy to obtain an analytical five-parameter dependence $A(t)$, which coincides in form with the empirically selected equation (1). The analytical solution allows us to give strict physicochemical interpretation of the observed rate constants k_{cis} and k_{trans} (Eqs. (3)–(6)):

$$k_{cis} = 0.5(\sigma + \delta), \quad (3)$$

$$k_{trans} = 0.5(\sigma - \delta), \quad (4)$$

$$\sigma = k_t + k_{-t} + k_c, \quad (5)$$

$$\delta = [\sigma^2 - 4k_c k_t]^{1/2}. \quad (6)$$

Using Eqs. (3)–(6) it is possible to calculate the elementary rate constants from the experimentally determined k_{cis} and k_{trans} . An unambiguous solution, however, requires an additional condition that correlates the elementary rate constants with the functional dependence. This condition is an expression for

the equilibrium constant of *cis–trans* isomerization. In accordance with the Van't Hoff isotherm equation

$$\frac{k_t}{k_{-t}} = K = \exp\left(-\frac{\Delta G^\circ}{RT}\right), \quad (7)$$

ΔG° equals the difference between the standard Gibbs energies of the *cis* and *trans* isomers of ArNOO, $G_c^\circ - G_t^\circ$. These values were calculated quantum-chemically in the M06L/6-311 + G(d,p) approximation, which ensures reliable calculation of the energy characteristics of aromatic nitroso oxides with an accuracy of high-level CCSD(T) calculations [17].

To find the elementary rate constants of stages from the effective constants, Eqs. (3)–(7) were transformed into the system of equations (8):

$$\begin{cases} k_c + k_t + k_{-t} = k_{cis} + k_{trans} \\ k_c k_t = k_{cis} k_{trans} \\ k_t = k_{-t} K. \end{cases} \quad (8)$$

Of the three algebraic equations with three unknowns, it is easy to obtain a quadratic equation with respect to one of the elementary rate constants. The positive root of the quadratic equation is the desired rate constant, substituting which into the equations of system (8), we found the remaining constants. The elementary rate constants k_t , k_{-t} , and k_c were calculated for all nitroso oxides over the entire temperature range of our experiments. The temperature dependence of the equilibrium constant $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ was included in calculation in the approximation of constant enthalpy and entropy of *cis–trans* isomerization. The calculated constants of the elementary stages are presented in Table 2.

The calculated elementary rate constants describing the decay of aromatic nitroso oxide isomers allow us to draw some conclusions. First, *ortho*-cyclization wins the competition and prevails over the isomerization of the *cis* isomer to the *trans* form, $k_c \gg k_{-t}$. As $k_c \gg k_t$, the expressions for the effective rate constants are significantly simplified: $k_{trans} \approx k_t$, $k_{cis} \approx k_c + k_{-t} \approx k_c$. The contribution of the isomerization of the *cis* isomer to the total rate of its decay is small in nitroso oxides

Iib, **Iic**, and **Iif**; in **Iia** and **Iie**, it is ~10%; and only in **Iid** it reaches ~20%. For this reason, the observed activation energies E_{cis} and E_{trans} are close to the activation energies of the corresponding elementary stages. Secondly, the theoretical estimates of the activation barriers of the stages of Scheme 2 indicate that ΔH^\ddagger of *cis*–*trans* isomerization are determined quite reliably: the observed deviation from the experimental data is random, and the average absolute deviation is 4.6 kJ/mol. The energy barrier of the *ortho*-cyclization of **Iia**–**Iif** is systematically overestimated by an average of 8.7 kJ/mol in calculations in the M06L/6-311 + G(*d,p*) approximation. Although the absolute value of the error is small, the theory predicts that the ratio of rate constants ($k_t, k_{-t} > k_c$) will be different from the experimentally observed ratio ($k_t, k_{-t} < k_c$). This circumstance should be taken into account further in the theoretical analysis of the reactivity of aromatic nitroso oxides.

CONCLUSIONS

The cascade transformations occurring during photo-oxidation of aromatic azides and including a chain of highly active intermediates: nitrene–nitroso oxide–nitrile oxide lead to the formation of various heterocyclic structures [12, 13, 23, 32] depending on the structure of the starting aryl azide, in particular, on the nature of substituent in the aromatic ring. The aromatic system can be a potential trap for the nitrile oxide function; therefore, here we studied the kinetics of the decay of nitrile oxide precursors—*cis* and *trans* isomers of nitroso oxides **Iia**–**Iic** containing an aromatic substituent in the *para* position. The rate constants of the reversible isomerization of the *trans* conformers to the corresponding *cis* form and of *ortho*-cyclization of the *cis* isomers, forming nitrile oxides, were determined. The presence of a phenyl fragment in the substituent affects the reactivity of the isomers of ArNOO, as indicated by a comparison of the effective rate constants for the compounds and nitroso oxides that are structurally similar but contain aliphatic substituents (Table 1). However, the observed effect is insignificant, which generally agrees with the conclusions of [24] made on the basis of DFT modeling of *ortho*-cyclization of some substituted aryl nitroso oxides. The three-stage mechanism of the decay of ArNOO makes it possible to obtain an analytical solution to the system of differential equations describing the joint decay of the *cis* and *trans* isomers. This circumstance significantly expands prospects for kinetic analysis of the reactivity of ArNOO, in particular, for calculation of elementary rate constants for all stages of the mechanism of nitroso oxide decay using experimental rate constants (Table 2). Another possibility is currently being examined in our laboratory, namely, the use of spectral and kinetic data of flash photolysis measurements for separate determination of the extinction coefficients of ArNOO isomers.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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