==== **PEROXIDES-XI** ====

Effect of the Structure of Reactants on the Reaction Rate Constants of Aromatic Nitroso Oxides with Olefins

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Abstract—The reactivity of phenylnitroso oxide, (*p*-methylphenyl)nitroso oxide, (*p*-nitrophenyl)nitroso oxide, (*m*-nitrophenyl)nitroso oxide, and (*p*-bromophenyl)nitroso oxide toward a number of olefins in acetonitrile at room temperature was studied using flash photolysis. It was found that the reaction rate constant decreased with decreasing energy of a molecular orbital with a maximum contribution from the atomic orbitals of carbon atoms in the C=C bond of olefins. This, along with a positive slope of the Hammett function for the reactions of substituted phenylnitroso oxides with 1-hexene and styrene, suggest an electrophilic character of these species. The temperature dependence of the rate constant of the reaction of phenylnitroso oxide with 1-hexene was studied: $\log A = 7.9 \pm 0.4$ [l mol^{-1} s^{-1}]; $E_a = 38 \pm 2$ kJ/mol.

INTRODUCTION

Nitroso oxides are formed in the reaction of triplet nitrenes with oxygen in the course of photooxidation of aromatic azides (**I**) [1–6]:
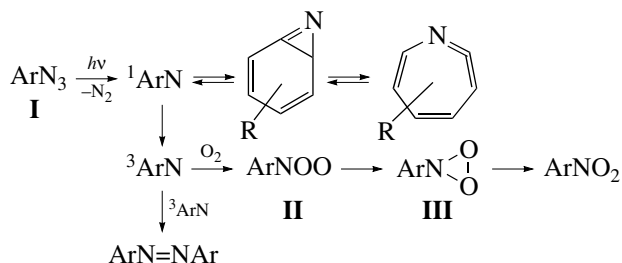
Ar = C$_6$H$_5$ (**a**), *para*-MeC$_6$H$_4$ (**b**), *para*-O$_2$NC$_6$H$_4$ (**c**), *meta*-O$_2$NC$_6$H$_4$ (**d**), *para*-MeOC$_6$H$_4$ (**e**), *para*-BrC$_6$H$_4$ (**f**)

Scheme.

A side reaction of primary photolysis products (singlet nitrenes) is their equilibrium conversion through benzazirines into dehydroazepines [1]. The presence of strong electron-acceptor substituents (such as NO$_2$) at the benzene ring reduced the probability of this reaction path to a minimum, and the singlet nitrene was almost completely converted into the triplet nitrene [2]. Triplet nitrenes undergo recombination to azobenzenes or react with molecular oxygen to form nitroso oxides (**II**). Sawaki and coauthors [4–6], who used the tracer method, found that nitroso oxides underwent unimolecular conversion into corresponding nitro compounds, probably through dioxaziridines (**III**), in the absence of oxygen scavengers from the system. Indeed, in a study of the reaction kinetics of decay of nitroso oxides **IIa–IIc** and **IIf** in acetonitrile, we found that they were con-

sumed in unimolecular reactions, and the rate constants measured at room temperature lay in the range 0.092–0.24 s^{-1} [7, 8].

The kinetics of the reactions of nitroso oxides with organic compounds has not been adequately studied. Sawaki and coauthors [4–6] studied the relative reactivities of compounds **IIa**, **IIc**, and **IIe** in reactions with aromatic and aliphatic hydrocarbons, sulfides, sulfoxides, nitrobenzenes, and olefins; in these reactions, arylnitroso oxides exhibited electrophilic properties.

There is no published information on the absolute rate constants of the reactions of nitroso oxides with organic compounds. In this study, we studied the kinetics of the reactions of nitroso oxides **IIa–IId** and **IIf** with a number of olefins in acetonitrile using flash photolysis with high-speed spectrophotometric detection. This is the first study in a series of studies on the reactivity of aromatic nitroso oxides with organic compounds from various classes.

EXPERIMENTAL

Acetonitrile was purified in accordance with a well-known procedure [9]. Azide **Ia** was synthesized according to Lindsay and Allen [10], whereas azides **Ib–Id** and **If** were synthesized according to Smith and Boyer [11]. Azides **Ia**, **Ib**, and **If** were distilled in a vacuum; compounds **Ic**, **Id**, and stilbene were recrystallized from ethanol. The other olefins were purified by distillation, if required, at a reduced pressure.

The kinetic experiments were performed using a flash photolysis system with spectrophotometric detection; the design of this system was described elsewhere [12]. An IFP 5000-2 lamp served as the photolytic source, the maximum pulse energy was 400 J at $U = 5$ kV,

C = 32 μF, and ~90% of the light energy was emitted within 50 μs. The reactor was a quartz cell with optical path length l = 10 cm and an inner diameter of ~1 cm. To prevent azide degradation under exposure to the 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 flash photolysis of the arylazide–olefin–acetonitrile–air (O$_2$ in the case of compounds **Ic** and **Id**) system was performed with filtered light (UFS-2 light filter; transmission region at $\lambda = 270–380$ nm). The initial concentration of aryl azides was $(0.5–2) \times 10^{-4}$ mol/l. The concentration of olefins was varied over the range $1 \times 10^{-5}–0.2$ mol/l. The reaction kinetics were monitored by measuring a decrease in the absorbance of nitroso oxides at a wavelength of 420 nm in the case of **IIa** and **IIb**, 410 nm in the case of **IIf**, and 400 nm in the case of **IIc** and **IId**.

RESULTS AND DISCUSSION

Spectroscopic Properties and the Kinetics of Consumption of Nitroso Oxides

In the flash photolysis of acetonitrile solutions of azides **Ia**, **Ib**, and **If** in the presence of oxygen, a signal was detected in the wavelength region 350–460 nm; the intensity of this signal decreased in a few seconds. The signal was absent if the system was preliminarily blown with argon. Thus, the observed absorbance corresponds to nitroso oxides **IIa**, **IIb**, and **IIf**. Their absorption maximums are at 410, 415, and 420 nm, respectively.

In the flash photolysis of deaerated solutions of compounds **Ic** and **Id**, a substance that absorbs light in the wavelength range 350–460 nm accumulated during the time of a light pulse. Taking into account the above-mentioned high probability of generation of triplet nitrenes in the photolysis of azides with strong electron-acceptor substituents, we can conclude that this substance is a corresponding azobenzene, the recombination product of triplet nitrenes (see the scheme). In solutions saturated with oxygen, this reaction was inhibited by the interaction of triplet nitrenes with O$_2$.

In the specified wavelength range, a signal was detected, which corresponds to **IIc** or **IId**. The optical spectrum of **IIc** contains two absorption maximums with approximately equal intensities at 375 and 420 nm, whereas the absorption maximum of compound **IId** lies at 395 nm. The consumption of compounds **IIc** and **IId** occurred in accordance with the first-order rate law.

It is most likely that the unimolecular consumption of **IIa**–**IId** and **IIf** was due to their isomerization into dioxaziridines (scheme). Table 1 summarizes the rate constants of nitroso oxide consumption.

Kinetics of the Interaction of Nitroso Oxides with Olefins

In the presence of olefins, the lifetimes of nitroso oxides decreased with increasing olefin concentration, whereas the rate of their consumption was described by a first-order rate equation (Fig. 1). The dependence of the effective rate constants (k_{eff}) of decay of nitroso oxides on the concentration of olefins was linear (Fig. 2). The absolute rate constants of reactions of nitroso oxides with olefins, k_{olef}, were determined from the slopes of these functions (Table 1). It is of interest that, in the case of **IIa**, **IIb**, and **IIf**, intercepts on the ordinate axis (they are given in parentheses in Table 1), that is, the effective rate constants in the absence of olefins, as a rule, are higher than the rate constants of unimolecular consumption of nitroso oxides (italicized in Table 1); they are lower in the case of **IId** and **IIc**, and they have a negative value for compound **IId**. As is obvious from the absolute errors, this fact is not due to an experimental error; it is likely that this is a regularity, which invites further investigation. As a working hypothesis, we assume that this regularity is related to the *syn–anti* conformation equilibrium of nitroso oxides. Only one (presumably, *anti*) conformer is involved in reaction with an olefin.

The temperature dependence of the rate constant of the reaction of compound **IIa** with 1-hexene was studied over the temperature range 293–333 K:

T, K	293	304	313	323	333
k_{olef}, l mol^{-1} s^{-1}	0.10 ± 0.01	0.27 ± 0.02	0.43 ± 0.02	0.74 ± 0.04	1.69 ± 0.06

From these data, we found
$\log A = 7.9 \pm 0.4$ [l mol^{-1} s^{-1}], and $E_a = 38 \pm 2$ kJ/mol.

The activation energy obtained is consistent with the activation energies (30–40 kJ/mol) of the reaction of peroxyl radical addition to a double bond [13].

The effect of the structure of test olefins on the rates of their reactions with nitroso oxides was characterized by a correlation between reaction rate constants and the energies of molecular orbitals (MOs) with a maximum contribution of the atomic orbitals (AOs) of the carbon atoms of a C=C bond, ε_π. The values of ε_π were calcu-

lated by the MP2/6-31G(d) nonempirical method for compounds **1**–**12** with the use of the GAMESS program [14]. In terms of Koopman's theorem, these energies with opposite signs are equal to the corresponding ionization potentials (IPs). With the use of olefins **1**, **3**, **5**, **7**, **8**, and **12** with known experimental IPs [15] as an example, a good agreement between calculated and experimental data was demonstrated (Table 2); this suggests that the values of ε_π for the other olefins are reliable. Figure 3 shows $\log k_{olef}$ as a function of ε_π for compound **IId**. Analogous functions were observed in

Table 1. Rate constants of the reactions of nitroso oxides with olefins $k_{\text{olef}} \times 10^{-2}$, l mol^{-1} s^{-1} [7, 8]*

Olefin	Nitroso oxide				
	IIa	**IIb**	**IIc**	**IId**	**IIf**
–	*0.10 ± 0.01*	*0.16 ± 0.01*	*0.092 ± 0.003*	*0.58 ± 0.07**	*0.24 ± 0.02*
Stilbene (**1**)	15.0 ± 0.4	11.5 ± 0.6	440 ± 20	310 ± 10	–
	(0.110 ± 0.007)	(0.196 ± 0.009)	(−0.4 ± 0.2)	(0.4 ± 0.2)	–
Styrene (**2**)	2.6 ± 0.1	1.60 ± 0.04	120 ± 3	107 ± 4	8.1 ± 0.2
	(0.15 ± 0.03)	(0.33 ± 0.01)	(−0.7 ± 0.8)	(−1 ± 2)	(0.47 ± 0.04)
Tetramethylethylene (**3**)	1.4 ± 0.1	1.26 ± 0.03	173 ± 1	66.5 ± 0.5	–
	(0.9 ± 0.2)	(0.9 ± 0.1)	(−7.3 ± 0.8)	(−1.8 ± 0.2)	–
Allylbenzene (**4**)	0.155 ± 0.004	0.093 ± 0.002	3.1 ± 0.2	3.5 ± 0.5	–
	(0.22 ± 0.01)	(0.24 ± 0.01)	(−0.1 ± 0.2)	(0.64 ± 0.02)	–
1-Hexene (**5**)	0.112 ± 0.002	0.072 ± 0.002	3.5 ± 0.1	2.3 ± 0.1	0.286 ± 0.005
	(0.154 ± 0.02)	(0.27 ± 0.01)	(−0.2 ± 0.2)	(0.4 ± 0.2)	(0.42 ± 0.01)
Allyl acetate (**6**)	0.092 ± 0.005	–	–	1.32 ± 0.06	–
	(0.22 ± 0.01)	–	–	(0.6 ± 0.1)	–
Allyl alcohol (**7**)	0.172 ± 0.005	–	–	1.3 ± 0.1	–
	(0.12 ± 0.02)	–	–	(1.0 ± 0.3)	–
Allyl bromide (**8**)	0.086 ± 0.003	0.086 ± 0.003	–	0.73 ± 0.01	–
	(0.13 ± 0.01)	(0.16 ± 0.03)	–	(0.47 ± 0.05)	–
Allyl butyl ether (**9**)	0.023 ± 0.001	–	–	0.231 ± 0.009	–
	(0.143 ± 0.003)	–	–	(0.38 ± 0.02)	–
Allyl vinyl ether (**10**)	–	–	–	0.023 ± 0.006	–
	–	–	–	(0.43 ± 0.02)	–
3-Octen-2-one (**11**)	0.037 ± 0.001	–	–	0.169 ± 0.002	–
	(0.290 ± 0.004)	–	–	(0.39 ± 0.01)	–
cis-1,2-Dichloroethylene (**12**)	0.0052 ± 0.0003	–	0.030 ± 0.001	0.023 ± 0.001	–
	(0.160 ± 0.003)	–	(0.170 ± 0.008)	(0.46 ± 0.05)	–

Note: The solvent is acetonitrile; $T = 295$ K.

    * The effective rate constants of nitroso oxide consumption extrapolated to zero olefin concentration are given in parentheses.

    ** The rate constant determined in this study.
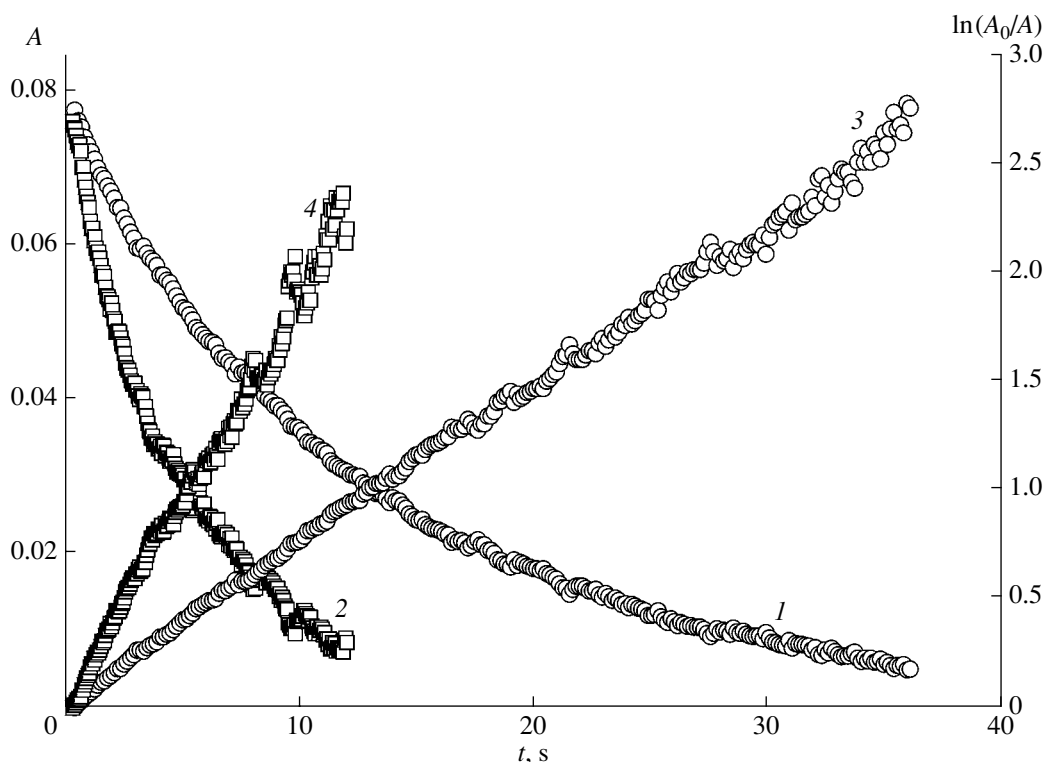
Fig. 1. Decay curves for the absorbance of **IIa**: (*1*) in the absence of additives, (*2*) in the presence of olefin **5** (8×10^{-3} mol/l), and (*3*, *4*) their semilogarithmic anamorphoses. Acetonitrile; [**Ia**] = 1.25×10^{-4} mol/l; air; $T = 295$ K.

all the test nitroso oxides; that is, the rate constant decreased with the absolute value of ε_π. This is indicative of electron-density transfer from the π (C=C) bond of an olefin to a nitroso oxide at a rate-limiting step of the reaction. Note that the rate constants for olefins **9–12** or **3** and **12** in the case of nitroso oxide **IIc** drop out of the correlation. The treatment of the resulting functions by the least-squares method resulted in the following expressions:

$$\log k_{\text{olef}} = (9.1 \pm 0.5) + (0.82 \pm 0.05)\varepsilon_\pi, \text{ [l mol}^{-1}\text{ s}^{-1}\text{]}$$

$$r = 0.990 \text{ for } \textbf{IIa};$$

$$\log k_{\text{olef}} = (9.0 \pm 0.8) + (0.82 \pm 0.08)\varepsilon_\pi, \text{ [l mol}^{-1}\text{ s}^{-1}\text{]}$$

$$r = 0.980 \text{ for } \textbf{IIb};$$

$$\log k_{\text{olef}} = (11.6 \pm 0.5) + (0.93 \pm 0.05)\varepsilon_\pi, \text{ [l mol}^{-1}\text{ s}^{-1}\text{]}$$

$$r = 0.997 \text{ for } \textbf{IIc};$$

$$\log k_{\text{olef}} = (12.0 \pm 0.8) + (1.00 \pm 0.08)\varepsilon_\pi, \text{ [l mol}^{-1}\text{ s}^{-1}\text{]}$$

$$r = 0.980 \text{ for } \textbf{IIf}.$$

The dependence of the rate constants on the electron properties of substituents at the aromatic nucleus of nitroso oxides was obtained using olefins **2** and **5** as examples. The plot of $\log k_{\text{olef}}$ as a function of the σ constants of constituents according to the Hammett relation [16] exhibited a positive slope (Fig. 4) ($\rho = 2.09 \pm 0.09$, $r = 0.997$ for **2** and $\rho = 1.80 \pm 0.08$, $r = 0.997$ for **5**). The

introduction of an electron-acceptor substituent into the benzene ring of a nitroso oxide increased the rate of its reaction with olefins; this fact is also indicative of an electrophilic character of nitroso oxides.

Thus, we studied the reactivities of aromatic nitroso oxides **IIa–IId** and **IIf** in interactions with a number of olefins. We found that the reaction rate constant

**Table 2.** Experimental and calculated ionization potentials (IPs) of olefins

Olefin	IP, eV	
	experimental [15]	calculated
1	7.80 ± 0.02 (*cis-*)	7.75
	7.70 ± 0.03 (*trans-*)	7.34
2	8.43 ± 0.06	8.11
3	8.27 ± 0.01	8.59
5	9.46 ± 0.05	9.56
7	9.67 ± 0.05	9.85
8	9.96	10.10
12	9.66 ± 0.01	9.94

k_{eff}, s^{-1}
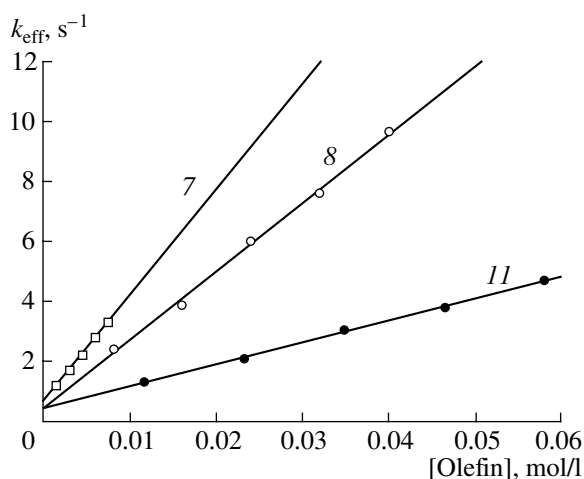
Fig. 2. Dependence of the effective rate constant of consumption of compound **IId** on the concentration of olefins (acetonitrile; oxygen; [**Id**] = 5×10^{-5} mol/l; λ = 400 nm; 295 K). Line numbers correspond to olefin numbers in Table 1.

$\log k_{\text{olef}}$ [l mol^{-1} s^{-1}]
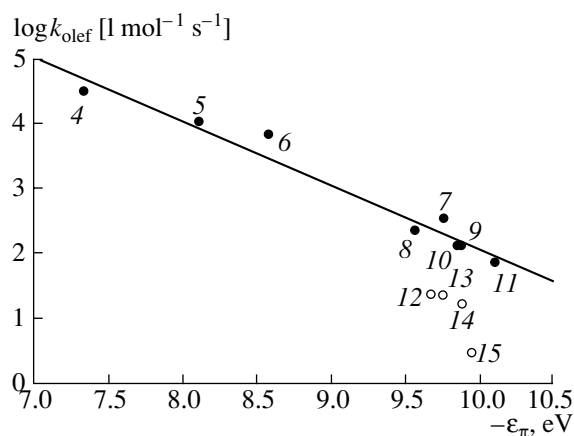
Fig. 3. Dependence of the rate constants of reactions of nitroso oxide **IId** with olefins on the energy of the molecular orbital with a maximum contribution from the atomic orbitals of the carbon atoms of a C=C bond in olefins (acetonitrile; 295 K; numbers correspond to olefin numbers given in Table 1).

$\log k_{\text{olef}}$ [l mol^{-1} s^{-1}]
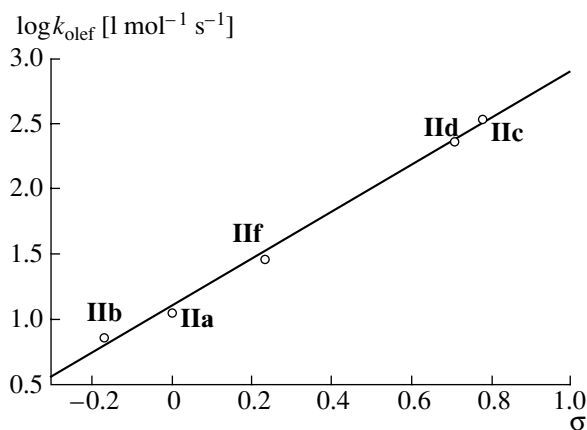
Fig. 4. Dependence of the rate constants of reactions of nitroso oxides XPhNOO with olefin **5** on the electron properties of substituent X in accordance with the Hammett equation (acetonitrile; 295 K).

decreased with decreasing energy of the MO that has a maximum contribution of the AOs of the carbon atoms of a C=C bond in olefins. Along with a positive slope of the Hammett relation for the reactions of substituted arylnitroso oxides with compounds **2** and **5**, this fact is indicative of an electrophilic character of these species. Our results are consistent with data published by Sawaki and coauthors [4–6], who compared nitroso oxides with electrophilic peroxyl radicals.

ACKNOWLEDGMENTS

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