

Reactivity of Arylnitroso Oxides to Triphenylphosphine

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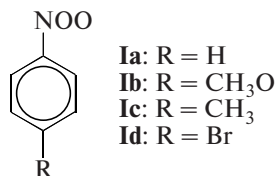
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Abstract—The kinetics of reactions between phenylnitroso oxide, 4-CH₃O-, 4-CH₃-, or 4-Br-phenylnitroso oxide and triphenylphosphine in acetonitrile at 295 ± 2 K were studied using pulsed photolysis. Only *trans*-nitroso oxides enter this reaction. The rate constants of the reaction increase with increasing electron-acceptor properties of the substituent in the aromatic ring of nitroso oxide; they are on the order of 10⁵ to 10⁶ l mol⁻¹ s⁻¹. The extinction coefficient for *trans*-4-methylphenylnitroso oxide at 420 nm was estimated at 3.9 × 10³ l mol⁻¹ cm⁻¹.

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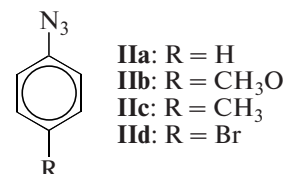
Nitroso oxides ArNOO are liable species generated by the reaction of triplet aromatic nitrenes with oxygen [1, 2]. They exist as geometric isomers (*cis* and *trans*) that differ in their spectral properties and reactivities. This difference made it possible to identify isomers in low-temperature matrices [3–5] and by pulsed photolysis in solutions at near-ambient temperatures and above [6, 7]. The death of both isomers obeys a first-order kinetic law; the rate constants of the reaction for *cis*-isomers are, as a rule, higher than for *trans*-isomers [7]. The death of nitroso oxides produces the corresponding nitroso- and nitrobenzene [8]. *trans*-Nitroso oxides enter the reaction with olefins, whereas the consumption rate laws for *cis*-isomers are virtually the same regardless of whether substrate additives are present or absent in the system [7].

In this work, we used pulsed photolysis to study the kinetics of reaction of nitroso oxides **Ia–Id** with triphenylphosphine (Ph₃P) in acetonitrile at 295 ± 2 K.



EXPERIMENTAL

Acetonitrile was purified by a known procedure [9]; triphenylphosphine was recrystallized from ethanol. Azides **Ia** and **Ic** were synthesized after [10] and azides **Ib** and **Id** after [11]. Azides **Ia** and **Ic** were distilled in vacuo; **Ib** was recrystallized from hexane and **Id** from ethanol.



Kinetic experiments were carried out on a pulsed photolysis setup of known design [12]. The photolytic source was an IFP 5000-2 lamp; the maximal pulse energy was 400 J at $U = 5$ kV, $C = 32$ μF, and ~90% of the light energy was irradiated in 50 μs. The reactor used was a quartz cell with the optical length $l = 10$ cm and the inner diameter ~1 cm. The filtered light (UFS-2 light filter; transmission range $\lambda = 270$ –380 nm) was used to perform pulsed photolysis of solutions of arylazides in acetonitrile saturated with atmospheric oxygen. Initial arylazide concentrations were 2.5×10^{-4} mol/l. Triphenylphosphine concentrations were varied within $(1.25$ – $500) \times 10^{-6}$ mol/l.

RESULTS AND DISCUSSION

Kinetics of the Reaction between Arylnitroso Oxides and Triphenylphosphine

Pulsed photolysis of solutions of arylazides **IIa–IId** in the presence of oxygen generates corresponding *cis*- and *trans*-nitroso oxides. Absorbance decay rate curves for arylazides **Ia–Id** recorded in the wavelength range where both isomers absorb each consist of two components and are well described by the five-parameter biexponential equation [7]

$$A = A_{\infty} + A_0^I e^{-k^I t} + A_0^{II} e^{-k^{II} t}. \quad (1)$$

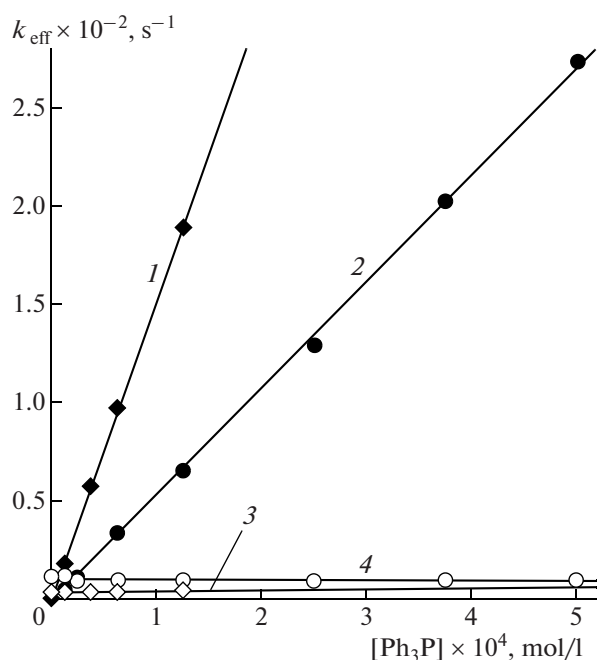


Fig. 1. Effective consumption rate constant for isomers of nitroso oxides **Ib** and **Ic** vs. triphenylphosphine concentration: (1) *trans*-**Ic**, (2) *trans*-**Ib**, (3) *cis*-**Ic**, and (4) *cis*-**Ib** (acetonitrile, 195 ± 2 K).

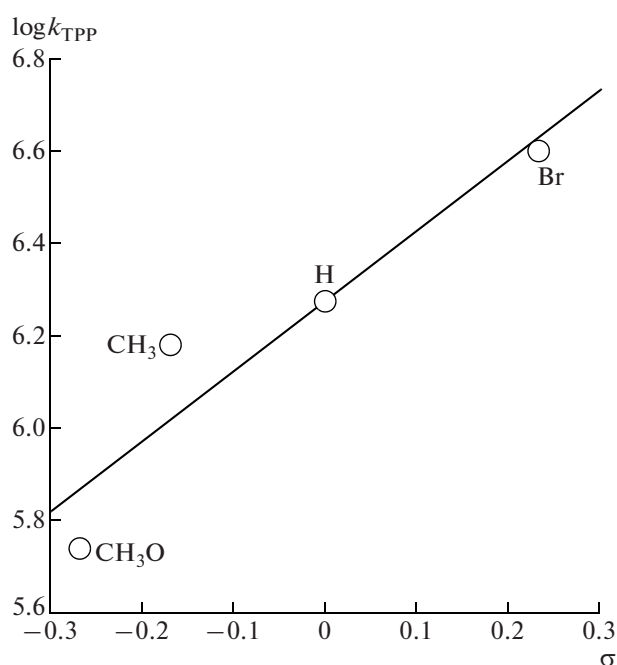


Fig. 2. Rate constant of the reaction of 4- $\text{XC}_6\text{H}_4\text{NOO}$ nitroso oxides with triphenylphosphine as a function of electronic properties of substituent X in the coordinates of the Hammett equation (acetonitrile, 295 ± 2 K).

Here, A_0^I , A_0^{II} , k^I , and k^{II} are initial absorbances and consumption rate constants for the *cis*- and *trans*-isomer, respectively; and A_∞ is the final absorbance associated with the absorption by reaction products.

Triphenylphosphine strongly increases the consumption rate of *trans*-nitroso oxides but does not change the death rate of the *cis*-isomers (Fig. 1). From the slopes of k_{eff} versus substrate concentration plots

Experimental data for calculating extinction coefficients for the *trans*-**Ic** isomer in acetonitrile at 420 nm

Pulse no.	$[\text{Ph}_3\text{P}]_0 \times 10^5, \text{ mol/l}$	A_0^{II}	$k_0^{II}, \text{ s}^{-1}$
1	3.89	0.1585	58.8
2	3.66	0.1408	55.3
3	3.07	0.1346	46.3
1	6.75	0.1923	102
2	6.19	0.1743	93.5
3	6.05	0.1669	91.3
4	5.48	0.1497	82.8
1	13.5	0.1290	204
2	12.6	0.1277	191
3	12.2	0.1464*	184
4	11.7	0.1407*	177

* An increased pulse energy.

(Fig. 1), we found k_{eff} , the absolute rate constants of the reaction between *trans*-nitroso oxides **Ia–Id** and triphenylphosphine: 5.5×10^5 , 1.5×10^6 , 1.9×10^6 , and $4.0 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ for **Ib**, **Ic**, **Ia**, and **Id**, respectively; the determination error was ~10%. The rate constants have rather high values for all nitroso oxides studied. This means that nitroso oxides in *trans*-conformation are efficient oxidizers for triphenylphosphine. Positive slopes of $\log k_{\text{eff}}$ plots as a function of Hammett σ substituent constants in a nitroso oxide molecule [13] ($\rho = 1.5 \pm 0.4$; $r = 0.94$) are indicative of the electrophilic behavior of nitroso oxides in the reactions under consideration (Fig. 2).

Estimation of Extinction Coefficient for *trans*-4- CH_3 -Phenylnitroso Oxide

The high reactivity of *trans*-nitroso oxides to triphenylphosphine enabled us to estimate extinction coefficients for these species using *trans*-**Ic** as an example. We carried out the following experiment. Solutions of azide **Iic** in the presence of triphenylphosphine were photolyzed by several light pulses. Every time the nitroso oxide consumption rate curve was recorded at 420 nm. Processing this curve with the use of Eq. (1), we obtained the initial absorbance of *trans*-**Ic** and the effective rate constant of its death (table). The effective rate constant decreased from pulse to pulse as a result of triphenylphosphine consumption. From k_{eff}^I and the rate constants of the reaction of *trans*-**Ic** with

triphenylphosphine (see above), the triphenylphosphine concentration in the system is as follows: $k_{\text{eff}}^{\text{II}} = k_{\text{TPP}}[\text{Ph}_3\text{P}]$. Thus, once the amount of triphenylphosphine consumed in each set of experiments is known (table) and if it is consumed only in the reaction with *trans*-nitroso oxide, we can estimate the extinction coefficient of the latter. For this purpose, we summed up the initial absorbances for each set minus the last pulse and divided it by $\Delta[\text{Ph}_3\text{P}]$ and the optical path length (10 cm). $\varepsilon_{\text{trans-Ic}}$ values obtained in this way for the three sets of experiments specified in the table are as follows: 4.2×10^3 , 4.2×10^3 , and $3.2 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$; the average is $3.9 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 420 nm in acetonitrile ($\lambda_{\text{max}} = 425 \text{ nm}$ [7]). The only estimate of the extinction coefficient found in the literature refers to 4-aminophenylnitroso oxide at 495 nm in toluene–THF (1 : 1); this is $2.1 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ [14]. This estimate was made on the assumption that azide quantitatively converts to nitroso oxide when photolyzed in the presence of oxygen. This estimate is higher than the value we found for *trans-Ic*, probably because of the different structures of the two nitroso oxides and different parameters of the experiments.

To summarize, we have determined the reactivity to triphenylphosphine for a number of aromatic nitroso oxides. We found that *trans*-nitroso oxides react with this reducing agent with rate constants of about 10^5 to $10^6 \text{ l mol}^{-1} \text{ s}^{-1}$, whereas *cis*-isomers are inactive in this reaction.

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