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Influence of 1,3-dichloroacetone on the regularities of decay of arylnitroso oxides

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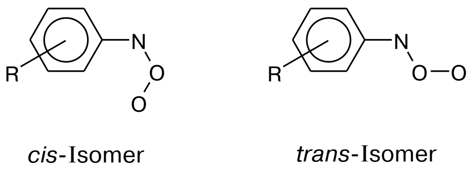
The decay kinetics of isomeric forms of a series of arylnitroso oxides in the presence of 1,3-dichloroacetone in acetonitrile was studied by the flash photolysis technique. The regularities observed are explained by the complex formation between the molecules of nitroso oxide and additive.

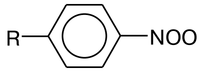
Key words: kinetics, flash photolysis, nitroso oxides, aryl azides, 1,3-dichloroacetone.

The reaction of triplet aromatic nitrenes with oxygen affords nitroso oxides (ArNOO),[1] *viz.*, labile species existing as geometric (*cis*- and *trans*-) isomers.



Isomers were detected by the matrix isolation methods[2—4] and time-resolved spectroscopy.[5,6] In the absence of oxidizable substrates, the isomeric forms of nitroso oxides decay according to the first-order kinetic law. The rate constants and activation parameters of this reaction in various solvents have been measured previously.[6]

The present work is devoted to the study of the influence of 1,3-dichloroacetone (DCA) on the regularities of consumption of the isomeric forms of nitroso oxides **1a—e** in acetonitrile. The decay kinetics of the isomers at different DCA concentrations was studied by the flash photolysis technique. The composition of the products of ArNOO transformations in the presence of DCA was studied by HPLC using nitroso oxide **1b** as an example.

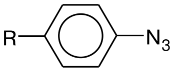


1a—e

R = H (**a**), OMe (**b**),
Me (**c**), Br (**d**), Cl (**e**)

Experimental

Acetonitrile was purified using a known procedure,[7] and DCA was sublimed for purification. Azides **2a—e** were used. Compounds **2a,c** (see Ref. 8) and **2b,d,e** (see Ref. 9) were synthesized according to described procedures. Azides **2a,c** were distilled *in vacuo*, azide **2b** was recrystallized from hexane, and compounds **2d,e** were recrystallized from ethanol. 4-Methoxynitrosobenzene[10] and 4-methoxynitrobenzene[11] were synthesized using published procedures.



2a—e

R = H (**a**), OMe (**b**),
Me (**c**), Br (**d**), Cl (**e**)

Kinetic studies were carried out on a flash photolysis setup of the known design.[12,13] An IFP 5000-2 lamp served as a photolytic source, the maximum energy of a pulse was 400 J at $U = 5$ kV, $C = 32$ μF, and ~90% light energy are irradiated within 50 μs. The reactor was a quartz cell with the optical path length l = 10 cm and internal diameter ~1 cm. Flash photolysis of a solution of aryl azide saturated with air oxygen in acetonitrile was carried out with the filtered light (UFS-2 light filter, transmission range λ = 270—380 nm). The initial concentration of aryl azides was $2.5 \cdot 10^{-4}$ mol L^{-1}. The DCA concentration was varied in the range $(7.5—625) \cdot 10^{-4}$ mol L^{-1}. The error of determination of the rate constants did not exceed 10%.

The transformation products of nitroso oxide **1b** in the presence of DCA were studied under the conditions of steady-state photooxidation of azide **2b**. A solution (10 mL) of azide **2b** in acetonitrile ($1 \cdot 10^{-3}$ mol L^{-1}) was placed in a temperature-maintained cylindrical quartz reactor. Photolysis was carried out with the light with λ = 270—380 nm (light filter UFS-2, mercury lamp DRT-400) at 293 K and permanent oxygen bubbling in the presence of DCA ($1.5 \cdot 10^{-3}$ or 0.02 mol L^{-1}) or without it. The distance from the reactor to the light source was ~20 cm. During the process, sampling was carried out at an interval of 5 min, and the overall reaction time was 20 min. The reaction mixtures were analyzed by HPLC on an Acme-9000

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liquid chromatograph (Young Lin Instrument) equipped with a two-wave UV—Vis detector; column Exsil Silica, mobile phase hexane—propan-2-ol (90 : 10 vol.%), flow rate of the mobile phase 2 mL $\min^{-1}$, ambient temperature of the column.

Results and Discussion

Kinetic regularities of the decay of arylnitroso oxides in the presence of DCA. Flash photolysis of solutions of aryl azides **2a—e** in the presence of oxygen generates *cis*- and *trans*-isomers of the corresponding nitroso oxides. The kinetic curves of the absorbance decrease for nitroso oxides **1a—e**, detected at the wavelengths at which the both isomers absorb the light, consist of two components and are well described by the five-parameter biexponential equation[6]

$$A = A_{\infty} + A_0^{cis}e^{-k^{cis}t} + A_0^{trans}e^{-k^{trans}t},$$

where A_0^{cis}, A_0^{trans}, k^{cis}, and k^{trans} are the initial absorbances and rate constants for the decay of *cis*- and *trans*-isomers, respectively; A_{∞} is the final absorbance caused by the absorption of the reaction products.

The influence of DCA on the kinetic regularities of isomer decay appears at a certain concentration of the additive in the system. The dependence of the apparent rate constant for the decay of the *cis*- and *trans*-forms of nitroso oxide **1b** (k_{app}) on the DCA concentration is shown in Fig. 1: the linear increase in the k_{app} value begins after some [DCA] value is achieved. Similar regularities were observed for other nitroso oxides except for **1d**, for which the apparent rate constants for isomer decay increase linearly in the whole range of additive concentrations ($(1.25—6.25) \cdot 10^{-3}$ mol L^{-1}). The concentration at which DCA begins to affect the decay kinetics of the nitroso oxides is $\sim 1.5 \cdot 10^{-3}$, $\sim 2.5 \cdot 10^{-3}$, and $\sim 2.5 \cdot 10^{-2}$ mol L^{-1} for **1c**, **1b,e**, and **1a**, respectively.

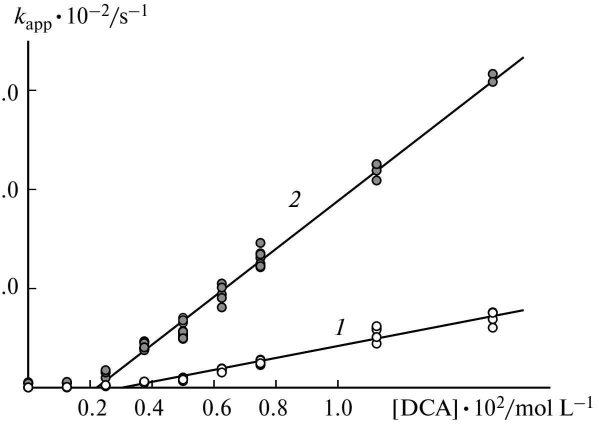


Fig. 1. Apparent rate constants for the decay of the *trans*- (*1*) and *cis*-isomers (*2*) of nitroso oxide **1b** (k_{app}) *vs* DCA concentration (acetonitrile, 295±2 K, detection wavelength 450 nm).

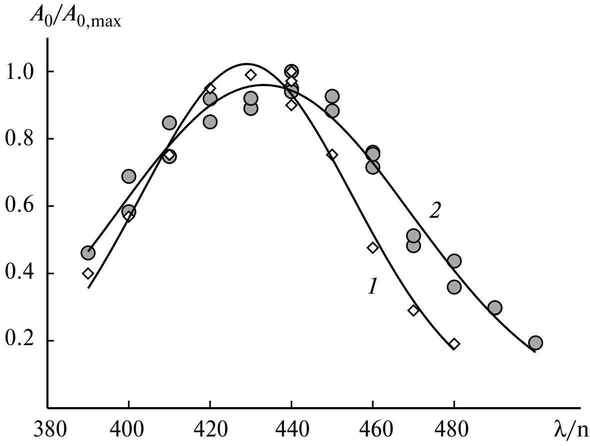


Fig. 2. Optical absorption spectra of the *cis*-form of nitroso oxide **1b** in acetonitrile at 295±2 K: [DCA] = 0 (*1*) and $1.25 \cdot 10^{-3}$ mol L^{-1} (*2*).

The regularities observed can be explained assuming that complex formation occurs between the components of the system under study. Let us assume that the following reactions occur under our experimental conditions:

$$ArNOO + (ClCH_2)_2C{=}O \rightleftharpoons ArNOO...(ClCH_2)_2C{=}O, \qquad (1)$$

$$ArNOO...(ClCH_2)_2C{=}O + (ClCH_2)_2C{=}O \longrightarrow Products. \qquad (2)$$

A complex between the nitroso oxide and additive is formed at the first stage. Then the complex reacts with the DCA molecule to form the final products. The DCA concentration, at which k_{app} begins to increase (see Fig. 1), corresponds to the conditions where the main fraction of ArNOO is bound in a complex with DCA. The further increase in [DCA] results in a linear increase in the apparent rate constant for nitroso oxide decay.

The complex formation of arylnitroso oxide with DCA is indicated by the broadening of the long-wavelength absorption band and the shift of its maximum in the electronic spectrum of the *cis*-isomer of nitroso oxide **1b** in the presence of DCA (Fig. 2). It should be mentioned that no changes in the spectral characteristics in the presence of DCA were observed for the *trans*-isomer.

In the region of high DCA concentrations, where almost all nitroso oxide exists in the bound state, we monitored the decay kinetics of the complex, and the decay rate of ArNOO was determined by the rate of reaction (2)

$$-d[ArNOO]/dt = -d[ArNOO...(ClCH_2)_2C{=}O]/dt = $$
$$= k_2[ArNOO...(ClCH_2)_2C{=}O][(ClCH_2)_2C{=}O].$$

Thus, the rate constants of the reaction of the complexes of the isomeric forms of nitroso oxides with DCA (k_2) were determined from the slope ratios of the linear plots presented in Fig. 1. The rate constant values are listed in Table 1. The reactivity of the complexes of the

Table 1. Decay rate constants of isomeric forms of nitroso oxides **1a—e** (k_2) in the presence of DCA (acetonitrile, 295±2 K)*

Isomer	$k_2 \cdot 10^{-2}$/L mol^{-1} s^{-1}				
	1a	**1b**	**1c**	**1d**	**1e**
cis	0.7	460	40	5.0	4.3
trans	0.2	120	7.9	1.7	1.8

* The error of determination of the rate constants did not exceed 10%.

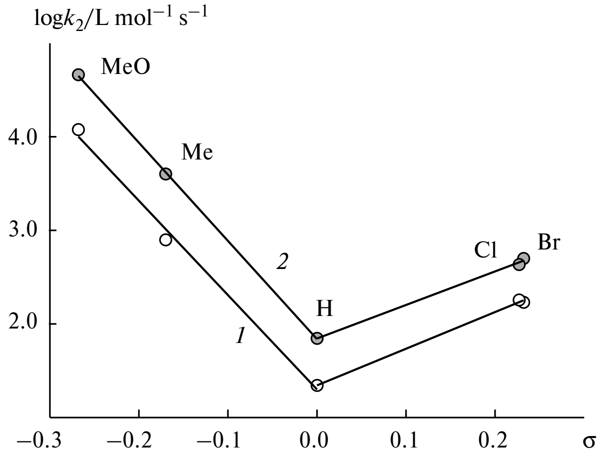


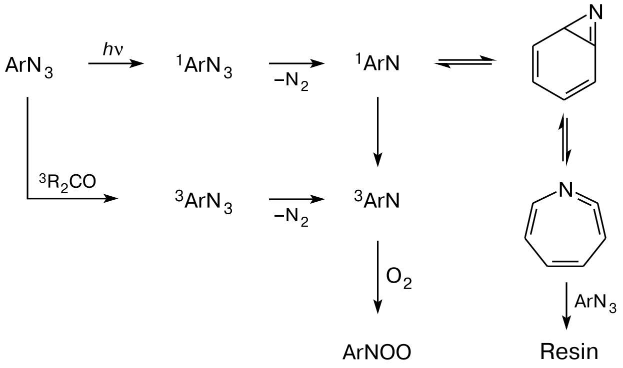
Fig. 3. Rate constants for the reaction of the complexes of the isomeric forms of nitroso oxides 4-XC_6H_4NOO (X = H, Me, MeO, Br, Cl) with DCA (k_2) *vs* electronic properties of the substituent X in the coordinates of the Hammett equation for the *trans*- (*1*) and *cis*-isomers (*2*) (acetonitrile, 295±2 K).

cis-isomers is higher than that of the *trans*-isomers and depends strongly on the nature of the substituent in the aromatic ring of the nitroso oxide, and both the electron-releasing and electron-withdrawing substituents increase the reaction rate constant (see Table 1). The dependence of logk_2 on the σ constants of substituents in the nitroso oxide molecule in the Hammett scale[14] has a V-like character (Fig. 3). A similar shape of the plots indicates the change in the mechanism of formation of the transition state due to different effects of the electron-releasing and electron-withdrawing substituents in the nitroso oxide molecule on the reaction course (nitroso oxide manifests biphilic properties). Remind that we consider the complex of nitroso oxide with the DCA molecule.

The regularities obtained seem rather unexpected for two reasons. First, we have earlier[15] studied the decay kinetics of nitroso oxides in acetone used as a solvent, and for nitroso oxide **1a** we obtained the rate constant of the same order as that in acetonitrile, while for 4-*N*,*N*-dimethylaminophenylnitroso oxide the constant turned out to be even lower than that in acetonitrile. That is, nitroso oxides do not react with unsubstituted acetone. Second, we have shown in several works[6,13,16,17] that only the *trans*-form of nitroso oxides is reactive in the reaction with the substrates (olefins, triphenylphosphine). The reactivity of the *cis*-form in the reaction with DCA is even several times higher than that of the *trans*-form (see Table 1).

Photooxidation products of 4-methoxyphenyl azide (2b) in the presence of DCA. The photooxidation of aromatic azides includes the following main stages (Scheme 1).[2,18]

Scheme 1



Singlet nitrenes are reversibly isomerized with ring expansion through the corresponding benzazirines to dehydroazepines or undergo intersystem crossing to form triplet nitrenes, which yield nitroso oxides in the presence of oxygen. At high azide concentrations, its reaction with dehydroazepine produces resins.[18] If the system contains a triplet sensibilizer, triplet nitrene can be obtained directly omitting the stage of formation of singlet nitrene and avoiding related secondary reactions.

To understand the mechanism of influence of DCA on the kinetic regularities of nitroso oxide decay, we studied the composition of the photooxidation products of azide **2b** in the presence and in the absence of the additive by HPLC. The photolysis of acetonitrile solutions of **2b** ($1 \cdot 10^{-3}$ mol L^{-1}) was carried out at 293 K with permanent oxygen bubbling. Three experiments were carried out at a DCA concentration of 0, $5 \cdot 10^{-3}$, and 0.02 mol L^{-1}. In all cases, the azide conversion was <50%. In all the three cases, the qualitative composition of the reaction mixture was the same: the products were the corresponding nitroso- and nitrobenzenes, which were determined by the retention times compared with the authentic samples (Table 2). The low yield of the products based on decomposed azide in the absence of DCA is due, most likely, to the fact that side reactions of resin formation occur at rather high azide concentration taken by us (see Scheme 1). No new compounds were observed in the studied system in the presence of DCA; however, the quantitative composition of the reaction mixture changed substantially. The fraction of azide, which

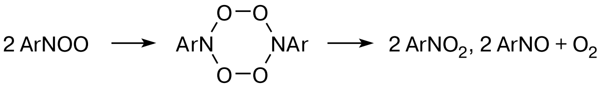
Table 2. Quantitative composition of the reaction mixture obtained by the photooxidation of azide **2b** in acetonitrile at 293 K and different durations of the reaction (*t*) ($[ArN_3]_0 = 1 \cdot 10^{-3}$ mol L^{-1})

$[DCA] \cdot 10^3$ /mol L^{-1}	*t* /min	$[ArN_3] \cdot 10^4$	$[ArNO] \cdot 10^5$	$[ArNO_2] \cdot 10^5$
			mol L^{-1}	
0	5	7.6	0.9	0.6
	10	6.6	1.4	1.4
	15	6.0	2.0	2.8
	20	5.3	2.8	4.2
5	5	7.8	2.0	2.2
	10	7.6	2.4	4.0
	15	6.4	3.0	5.8
	20	5.6	3.4	7.2
20	5	9.1	2.4	3.8
	10	7.8	3.0	7.6
	15	7.2	3.6	10.4
	20	5.8	4.1	15.8

decayed every moment, somewhat decreased with some increase in the yield of nitrosobenzene and a considerable increase in the yield of nitrobenzene (see Table 2).

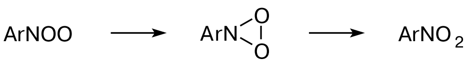
Nitroso and nitro compounds are typical photooxidation products of aromatic azides.[2,19–21] Their yield and ratio vary, depending on the reaction conditions. It has earlier been found[2] by flash photolysis that 4-aminophenylnitroso oxide is consumed bimolecularly with the rate constant close to the diffusion one. It is assumed that the bimolecular decay of nitroso oxides proceeds through the intermediate formation of dimeric peroxide, which decomposes to either two molecules of the nitro compound, or to two molecules of the nitroso compound and oxygen (Scheme 2).

Scheme 2



The parallel formation of nitroso- and nitrobenzene upon the photooxidation of azides can be explained using this mechanism. However, all nitroso oxides studied[6] decay in a monomolecular reaction, for example, in isomerization to nitrobenzene (Scheme 3).

Scheme 3



The occurrence of this reaction was proved by the method of labeled atoms.[22–24]

However, how is nitrosobenzene formed in this case? This very difficult question remains yet unanswered. An analysis of the results obtained in the present work suggests that DCA is involved somehow in the decay of nitroso oxides, but no new products are formed. The yields of ArNO and $ArNO_2$ increase non-proportionally in the presence of the additive in the system (see Table 2). In the case of the parallel formation of these products from nitroso oxides, one should expect a proportional increase in their yields in the presence of DCA. The conclusion that nitroso and nitro compounds are formed in different transformations of nitroso oxides was drawn[25] on the basis of analysis of the photooxidation products of azidostyrylquinolines and their hydrochlorides in ethanol. Perhaps, nitrosobenzene is not a product of nitroso oxide transformation but is formed in any secondary reaction. Then, based on the data presented in Table 2, one can assume that DCA sensitizes the formation of azide in the triplet state (see Scheme 1). This increases the yield of triplet nitrene, due to which the yield of nitroso oxide and, hence, nitrobenzene increases. Since no products of the reaction of nitroso oxide **1b** with DCA were found, the increase in the decay rates of the both forms of nitroso oxides in the presence of DCA detected by flash photolysis (see Fig. 1 and Table 1) is explained, probably, by catalysis of nitrobenzene formation from ArNOO.

Activation parameters of the decay of 4-methoxyphenylnitroso oxide (1b) in the presence of DCA. The temperature dependence of the decay rate constant for the isomers of nitroso oxide **1b** in the interval 276—325 K (ketone concentration $7.5 \cdot 10^{-3}$ mol L^{-1}) was studied by the flash photolysis technique. The apparent rate constants for the decay of the isomeric forms obtained at different temperatures were divided into this concentration and the k_2 values were determined. The dependence of $\log k_2$ on the inverse temperature is linear for the both isomers (Fig. 4). The following values of the activation parameters were obtained: $\log A = 11.1 \pm 0.2$, $E_a = 41 \pm 1$ kJ mol^{-1} (for *trans*-**1b**) and $\log A = 9.2 \pm 0.1$, $E_a = 26.0 \pm 0.8$ kJ mol^{-1} (for *cis*-**1b**). The earlier[6] determined activation parameters for the monomolecular decay of this nitroso oxide had the following values: $\log A = 11.4 \pm 0.2$, $E_a = 67.2 \pm 0.9$ kJ mol^{-1} (for *trans*-**1b**) and $\log A = 11.7 \pm 0.1$, $E_a = 60.5 \pm 0.3$ kJ mol^{-1} (for *cis*-**1b**). Thus, taking into account the results obtained in flash experiments and in experiments on studying the photooxidation products of azide **2b** in the presence of DCA, one can conclude that this ketone accelerates the isomerization of nitroso oxides to nitrobenzene, decreasing considerably the activation energy of this transformation for the both conformers. The activation entropy for the *trans*-isomer changes weakly, being at 293 K -34.9 J mol^{-1} K^{-1} in the absence of DCA and -40.6 J mol^{-1} K^{-1} in the presence of DCA. In the case of the *cis*-isomer, the changes are more significant: -29.2 and -77.0 J mol^{-1} K^{-1}, respectively.

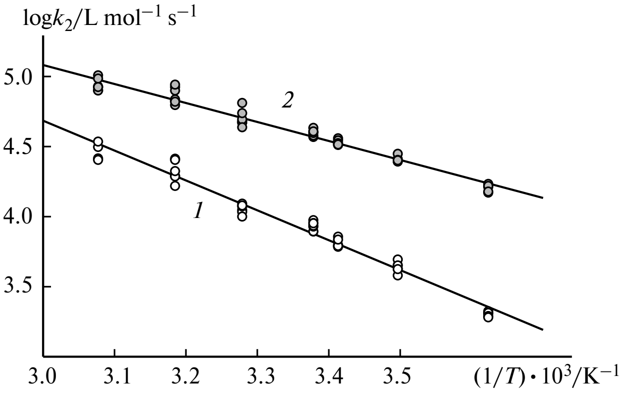
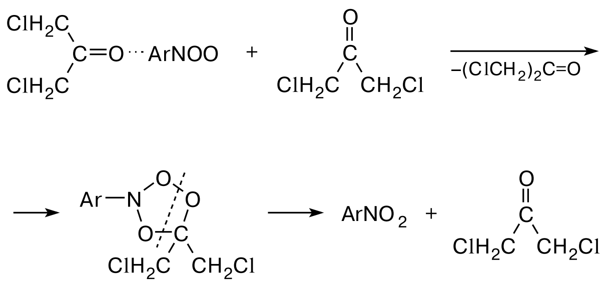


Fig. 4. Temperature dependences of the rate constant for the reactions of the *trans*- (*1*) and *cis*-isomers (*2*) of nitroso oxide **1b** bound in complexes with DCA (k_2) (acetonitrile, detection wavelength 450 nm).

Perhaps, an interaction similar to the addition of carbonyl oxides to the carbonyl group with the formation of "secondary" ozonide occurs in the system under study.[26] Then the occurring processes can be presented by Scheme 4. At first a complex of nitroso oxide with a DCA molecule is formed and reacts with the second ketone molecule to form an intermediate product of the type of "secondary" ozonide. The latter decomposes to nitrobenzene and ketone.

Scheme 4



Kinetics of the reaction of the complexes of the isomeric forms of 4-methoxyphenylnitroso oxide (1b) with triphenylphosphine. We have earlier[17] studied the reactivity of the isomeric forms of some arylnitroso oxides toward triphenylphosphine. Only the *trans*-isomers of nitroso oxides are involved in this reaction, and the rate constant is about 10^5—10^6 L mol^{-1} s^{-1}. Since the presence of DCA strongly changes the reactivity of the isomeric forms in the decay reaction, we decided to check how this additive would affect the kinetics of the reaction of ArNOO with triphenylphosphine. The studies were carried out by the flash photolysis technique for nitroso oxide **1b**. Such a concentration of DCA was used ($2.5 \cdot 10^{-3}$ mol L^{-1}) that the all nitroso oxide would be bound into a complex (see Fig. 1). The dependence of the apparent rate constant for the decay of the complexes of the isomeric forms of **1b** on the triphenylphosphine concentration was obtained (Fig. 5). It turned out that at first k_{app} for *trans*-**1b** somewhat increases and then remains unchanged with an increase in the phosphine concentration. A linear dependence of k_{app} on [Ph$_3$P] is observed for *cis*-**1b**, and its slope ratio gave the rate constant for the reaction of the *cis*-isomer of **1b** bound in a complex with triphenylphosphine: $4.5 \cdot 10^5$ L mol^{-1} s^{-1}. This value almost coincides with the earlier[17] measured rate constant for the reaction of the *trans*-form of **1b** with Ph$_3$P ($5.5 \cdot 10^5$ L mol^{-1} s^{-1}). Thus, some inversion of the reactivity of the isomeric forms toward the oxidized substrate under the action of DCA was observed. The nature of this phenomenon remains yet unexplained.

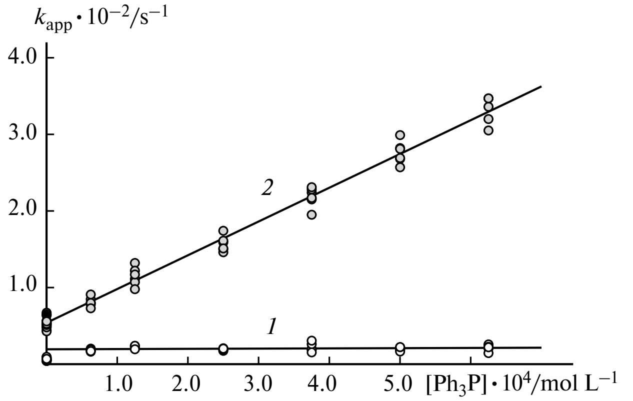


Fig. 5. Apparent rate constants for the decay of the *trans*- (*1*) and *cis*-isomers (*2*) of nitroso oxide **1b** (k_{app}) in the presence of DCA ($2.5 \cdot 10^{-3}$ mol L^{-1}) *vs* triphenylphosphine concentration (acetonitrile, 295±2 K, detection wavelength 450 nm).

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