ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 1, pp. 97–102. © Pleiades Publishing, Ltd., 2009.
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Kinetics of Reactions between Arylnitroso Oxides and Methyl Vinyl Ketone

E. M. Chainikova and R. L. Safiullin

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450054 Bashkortostan, Russia
e-mail: kinetic@anrb.ru

Received July 25, 2007

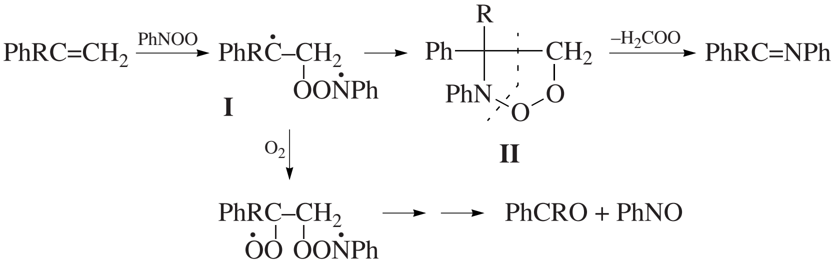
Abstract—The kinetics of the reactions of phenylnitroso oxide, (4-methylphenyl)nitroso oxide, (4-methoxyphenyl)nitroso oxide, 4-(*N*,*N*-dimethylamino)phenylnitroso oxide, (4-chlorophenyl)nitroso oxide, (4-bromophenyl)nitroso oxide, and (4-nitropenyl)nitroso oxide with methyl vinyl ketone in acetonitrile at 295 K was studied. With the use of 4-CH_3O–C_6H_4–NOO as an example, it was found that only the *trans* isomers of nitroso oxides entered into the reaction. The rate constants of the reactions of the *trans* isomers of nitroso oxides with methyl vinyl ketone were measured. A linear correlation between the logarithms of reaction rate constants and the electronic properties of substituents in the aromatic rings of nitroso oxides on the Hammett scale was established: $\rho = 1.11 \pm 0.08$; $r = 0.990$.

DOI: 10.1134/S0023158409010133

INTRODUCTION

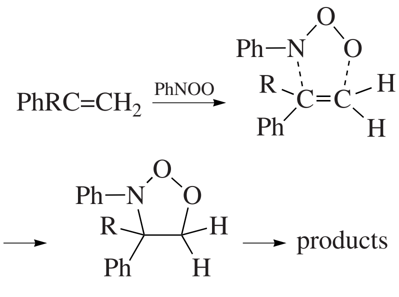
Nitroso oxides (ArNOO) belong to the class of 1,3-dipolar species. They are formed as intermediates by the interaction of triplet nitrenes with oxygen in the photooxidation of aromatic azides [1]. Previously, we used flash photolysis to study the effects of the nature of solvents and the structure of arylnitroso oxides on the reactivity and spectroscopic properties of these nitroso oxides [2–4]. In the absence of oxidation substrates, these species were consumed in unimolecular reactions. Chainikova et al. [4] found that nitroso oxides behaved as typical electrophiles in reactions with olefins: electron-acceptor substituents in the aromatic ring of a nitroso oxide and electron-donor substituents at the double bond of an olefin increased the rate constant of the reaction.

Ishikawa et al. [5] studied the reaction products of phenylnitroso oxide with styrene and α-methylstyrene and proposed the following mechanism:



Scheme 1.

It is believed that cyclic peroxide **II** is formed either in an intramolecular recombination of biradical **I** or by a single-step mechanism. In our opinion, it is most likely that the latter assumption is true because nitroso oxides in the ground singlet state are typical 1,3-dipoles, which are characterized by a [3+2]-cycloaddition reaction with dipolarophiles such as olefins [6]. Then, the course of the reaction can be represented by the following scheme:

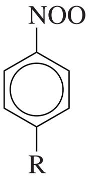


Scheme 2.

Our recent results suggest that the isomeric forms (*cis* and *trans*) of arylnitroso oxides can be separately identified in solutions at moderate temperatures using flash photolysis; the occurrence of these isomeric forms is due to the molecular structure of these species [7]:

Previously, this identification was possible only at low temperatures in matrices for 4-aminophenylnitroso oxide [8, 9] and 4-nitrophenylnitroso oxide [10] with the use of IR and UV spectroscopy. We obtained the electronic spectra, studied the kinetics of unimolecular decay of the isomeric forms of a number of arylnitroso oxides in solvents of different polarities, and measured the activation parameters of this reaction [7]. Using tetramethylethylene as an example, we found that mainly the *trans* isomer entered into the reaction with an oxidation substrate [7].

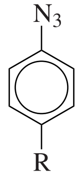
In this work, we used flash photolysis to study the kinetics of reactions of nitroso oxides **IIIa**–**IIIg** with methyl vinyl ketone in acetonitrile at 295 ± 2 K.



IIIa: R = H
IIIb: R = CH_3
IIIc: R = CH_3O
IIId: R = $(CH_3)_2N$
IIIe: R = Cl
IIIf: R = Br
IIIg: R = NO_2

EXPERIMENTAL

Acetonitrile was purified using a standard procedure [11]. Methyl vinyl ketone was purified by distillation. The flash photolysis of azides **IVa**–**IVg** in the presence of air or oxygen was used to generate the test arylnitroso oxides. Azide **IVa** was synthesized according to Lindsay and Allen [12]; compounds **IVb**–**IVg** were synthesized according to Smith and Boyer [13]. Compounds **IVa** and **IVb** were distilled in a vacuum; **IVe**–**IVg** were recrystallized from ethanol, and **IVc** was recrystallized from hexane; **IVd** was purified on a column with Silica Gel 60 from Merck (eluant: hexane–ethyl acetate (2–3 vol %)).



IVa: R = H
IVb: R = CH_3
IVc: R = CH_3O
IVd: R = $(CH_3)_2N$
IVe: R = Cl
IVf: R = Br
IVg: R = NO_2

Kinetic experiments were performed using a system for flash photolysis, which was described elsewhere [14]. The photolytic source was an IFP 5000-2 lamp; the maximum pulse energy was 400 J at U = 5 kV; C = 32 μF; ~90% light energy was emitted in 50 μs. The spectrophotometric unit of the system consisted of a DKSSh-150 xenon lamp as a continuous wave probe source with a system of quartz lenses and diaphragms for the formation of a probing beam, an MDR-4 monochromator, an FEU-97 photomultiplier tube, and an S9-8 storage oscilloscope. This system was equipped with a device for computer processing of pulse signals. After the precompensation of a constant component, a signal from the photomultiplier tube was amplified and transferred to the inlet of a digital oscilloscope, which operated in standby mode. The digitized signal was transferred to a computer through an IEEE-488 interface (GIPB). Kinetic curves were subjected to nonlinear regression analysis. The error in the determination of rate constants was no higher than 10%. The reactor was a thermostated quartz cell with an optical path length of l = 10 cm and an inner diameter of ~1 cm.

The flash photolysis of an aryl azide solution saturated with air (or oxygen in the case of **IVg**) was performed with filtered light (UFS-2 light filter; transmittance range λ = 270–380 nm). The initial concentration of aryl azides was (2.5–25) × 10^{-5} mol/l. The concentration of methyl vinyl ketone was varied over the range of (1.51–7.55) × 10^{-3} mol/l in the case of nitroso oxides **IIIa**–**IIIc** or (7.55–45.3) × 10^{-3} mol/l in the case of **IIId**.

RESULTS AND DISCUSSION

The electronic absorption spectra and the kinetics of decay of the isomeric forms of arylnitroso oxides in acetonitrile, benzene, and *n*-hexane in the absence of oxidation substrates were described in detail elsewhere [7]. The wavelengths of absorption maximums (in nm) in acetonitrile for *cis* and *trans* isomers, respectively, were 380 and 405 (**IIIa**), 390 and 425 (**IIIb**), 430 and 460 (**IIIc**), 500 and 600 (**IIId**), 375 and 405 (**IIIe**),[1] 380 and 415 (**IIIf**), and 380 and 420 (**IIIg**). The rate constant of decay of the *cis* form was higher than that of the *trans* form (see the table). The exception is provided by nitroso oxides **IIId** and **IIIg**. In the case of **IIId**, the *trans* form was consumed with a somewhat greater rate constant than the *cis* form. In the case of **IIIg**, both of the isomers exhibited the same stability, and they cannot be distinguished kinetically, although the absorption spectrum of this nitroso oxide in acetonitrile contains two maximums.

Using nitroso oxides **IIIc** and **IIIf** as an example, we demonstrated that isomeric forms exhibit different activities toward tetramethylethylene [7]. The rate constant of the reaction of the *trans* form was 64 l mol^{-1} s^{-1}. We failed to detect the interaction of the *cis* form of **IIIc** with tetramethylethylene under the experimental conditions. In the case of **IIIf**, the *cis* form reacted with tet-

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[1] The absorption maximums of **IIIe** were determined in this work.

Rate constants of decay of the isomeric forms of nitroso oxides [7], intercepts (k_0) in the axis of ordinates for the dependences of apparent rate constants of consumption of *trans* isomers on the concentration of methyl vinyl ketone, and the rate constants of reactions of the *trans* isomers with methyl vinyl ketone* ($T = 295 \pm 2$ K; acetonitrile)

ArNOO	k_{cis}, s^{-1}	k_{trans}, s^{-1}	k_0, s^{-1}	$k_{\text{MVK}} \times 10^{-2}$, l mol^{-1} s^{-1}
IIIa	1.19	0.10	0.11	1.60
IIIb	2.25	0.17	0.19	1.40
IIIc	11.3	0.37	0.33	1.00
IIId	150	260	–	–
IIIe	1.77**	0.15**	0.17	2.8
IIIf	1.45	0.14	0.17	3.0
IIIg	0.09***			15.0***

* Error in the determination of rate constants was no larger than 10%.
** Rate constants determined in this work.
*** Total values for both isomers.

ramethylethylene with a small rate constant of 9 l mol^{-1} s^{-1}, and the rate constant of the reaction of the *trans* form was 1.09×10^{-3} l mol^{-1} s^{-1}.

In the presence of methyl vinyl ketone, the lifetime of the *trans* form of nitroso oxide **IIIc** was shorter, whereas the lifetime of the *cis* form remained almost unchanged (Fig. 1). The kinetic curves of decay of the absorbance of **IIIc** were described by the five-parameter biexponential equation

$$A = A_\infty = A_0^{\text{I}} e^{-k_{\text{a}}^{\text{I}} t} + A_0^{\text{II}} e^{-k_{\text{a}}^{\text{II}} t}, \qquad (1)$$

where A_0^{I}, A_0^{II}, k_{a}^{I}, and k_{a}^{II} are the initial absorbances of the *cis* and *trans* isomers and the apparent rate constants of consumption of the *cis* and *trans* isomers, respectively, and A_∞ is the final absorbance due to the absorption of reaction products.

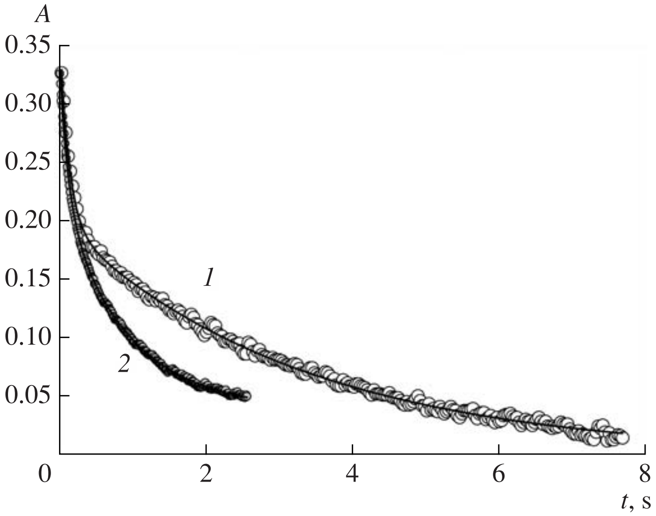

Fig. 1. Kinetic curves of consumption of nitroso oxide **IIIc** in acetonitrile measured at a wavelength of 440 nm and their theoretical description with Eq. (1): (*1*) in the absence of methyl vinyl ketone and (*2*) in the presence of methyl vinyl ketone (7.55×10^{-3} mol/l).

The apparent rate constant of consumption of the *cis* form remained unchanged within the limits of experimental error, whereas that of the *trans* form increased with the concentration of methyl vinyl ketone over the range used in this study (Fig. 2). From the slope of function (1) (Fig. 2), we determined the absolute rate constant of the reaction of the *trans* isomer of **IIIc** with methyl vinyl ketone (k_{MVK}) (see the table). The intercept in the axis of ordinates (k_0, Table 1) coincided with the rate constant of unimolecular decay of *trans*-**IIIc** to within the experimental error.

Analogously, we attempted to measure the reactivity of the isomeric forms of the other nitroso oxides toward methyl vinyl ketone. In the case of nitroso oxides **IIIa**,

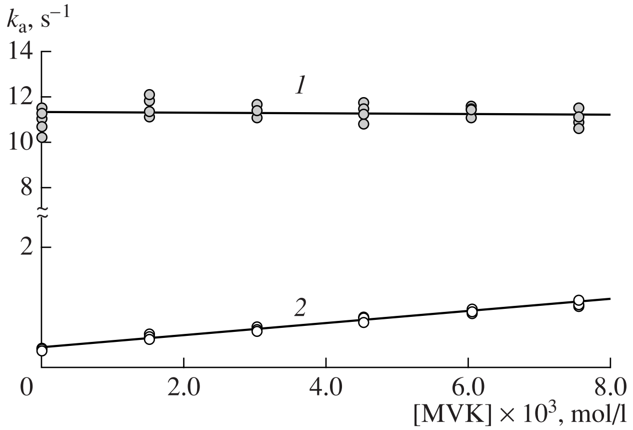

Fig. 2. Dependence of the apparent rate constants of consumption of the (*1*) *cis* and (*2*) *trans* isomers of nitroso oxide **IIIc** in acetonitrile on the concentration of methyl vinyl ketone.

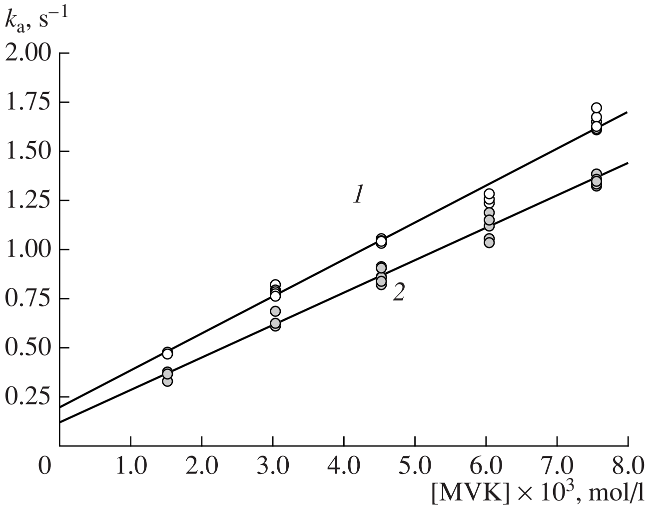

Fig. 3. Dependence of the apparent rate constants of consumption of nitroso oxide **IIIa** in acetonitrile on the concentration of methyl vinyl ketone: detection wavelength of (*1*) 400 and (*2*) 430 nm.

IIIb, **IIIe**, and **IIIf**, a decrease in the absorbance was observed at a wavelength of 400 nm, at which both of the isomers absorbed light. In the absence of a substrate, the kinetic curves consisted of two segments, whereas they cannot be adequately described by Eq. (1) upon the addition of methyl vinyl ketone ($(1.51–7.55) \times 10^{-3}$ mol/l) to the system. This is because the difference between the rate constants of decay of the isomeric forms of these nitroso oxides is not as great as in the case of **IIIc** (table), and the rate constants of consumption of two species become closer to each other in the presence of a substrate toward which one of the isomers is inactive and these species cannot be distinguished in terms of reactivity. The resulting kinetic curves are adequately described by the first-order equation

$$A - A_\infty = (A_0 - A_\infty)e^{-k_a t}. \qquad (2)$$

The rate constants thus calculated are overall values, and the apparent rate constants of consumption of *cis* and *trans* isomers contribute to these values. The dependence of these overall constants on the concentration of methyl vinyl ketone is linear (Fig. 3, straight line *1*). At $\lambda > 420$ nm, the kinetic curves of consumption of the *trans* isomers of **IIIa**, **IIIb**, **IIIe**, and **IIIf** in the pure forms are detected. Thus, the reaction rate constants of these species with methyl vinyl ketone can be measured over the above range. Figure 3 (straight line *2*) shows the dependence of the apparent rate constant of consumption of *trans*-**IIIa** on the concentration of methyl vinyl ketone. The intercept in the axis of ordinates is consistent with the rate constant of decay of the *trans* isomer of this nitroso oxide in the absence of active additives (see the table). Analogous dependences were obtained for nitroso oxides **IIIb**, **IIIe**, and **IIIf**. The table summarizes the rate constants of the reactions of *trans* isomers with methyl vinyl ketone. In our previous work [4], the intercepts in the dependences of the apparent rate constants of nitroso oxide consumption on olefin concentrations were inconsistent with the rate constants of unimolecular decay of these species. Previously [4], we assumed that this can be due to the fact that arylnitroso oxides occur in two isomeric forms, *cis* and *trans*. Now, this assumption becomes obvious. Indeed, we studied previously the kinetics of reactions of nitroso oxides **IIIa**, **IIIb**, **IIIe**, and **IIIf** with olefins at wavelengths of 410 and 420 nm, where the contribution of the *cis* isomer affected the overall process. As a result, we obtained an overestimated apparent rate constant of nitroso oxide consumption upon extrapolation to zero olefin concentration. In this case, the slope of functions obtained at different wavelengths changed insignificantly: 190 l mol^{-1} s^{-1} ($\lambda = 400$ nm) and 160 l mol^{-1} s^{-1} ($\lambda = 430$ nm) for the reaction of nitroso oxide **IIIa** with methyl vinyl ketone (Fig. 3). Thus, we can conclude that, previously [4], the rate constants of reactions of the *trans* isomers of nitroso oxides **IIIa**, **IIIb**, **IIIe**, and **IIIf** with olefins were estimated inadequately.

In the case of nitroso oxide **IIIg**, we failed to detect a difference between the reactivities of the isomeric forms toward methyl vinyl ketone. The resulting rate constant is given in the table.

The presence of a strong electron-donating substituent in the aromatic ring of **IIId** deactivates this nitroso oxide in a reaction with methyl vinyl ketone. Although, in this case, the concentration of the additive ($(7.55–45.3) \times 10^{-3}$ mol/l) was higher than the concentration used for other nitroso oxides by almost one order of magnitude, the kinetics of consumption of both of the isomers of **IIId** remained unchanged within the limits of experimental error as the methyl vinyl ketone content of the system was increased.

We obtained the dependence of the logarithms of the rate constants of reactions between the *trans* isomers of nitroso oxides and methyl vinyl ketone on the electronic properties of substituents in the aromatic rings of the nitroso oxides. As in the case of 1-hexene and styrene [4], the slope of $\log k_{\mathrm{MVK}}$ plotted as a function of the σ constants of substituents on the Hammett scale [15] was positive (Fig. 4), although its value ($\rho = 1.10 \pm 0.08$; $r = 0.990$) was lower by a factor of almost 2 (2.09 for styrene or 1.80 for 1-hexene).

Because nitroso oxides exhibit electrophilic properties in reactions with olefins [4], it would be expected that the acetyl substituent $CH_3C(O)$ at the double bond in the methyl vinyl ketone molecule would decrease the rate constant of the reaction. However, the obtained rate constants k_{MVK} are comparable with the rate constants for tetramethylethylene and they are higher than those for 1-hexene by one or two orders of magnitude [4]. Earlier [4], we characterized the effect of the structure of test olefins on the rate of their reactions with nitroso oxides using the correlation between the reaction rate

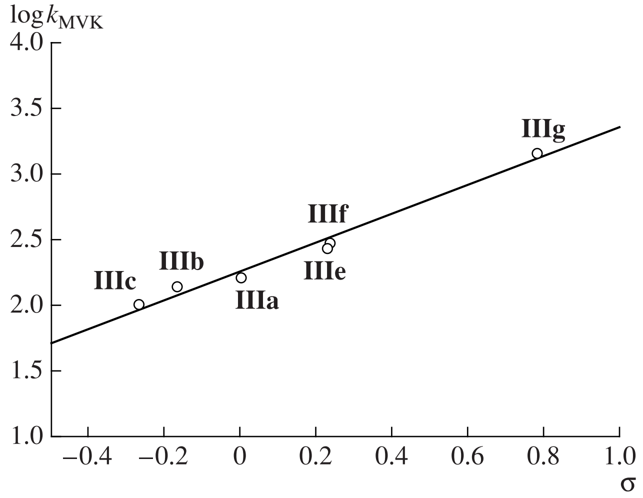

Fig. 4. Dependence of the rate constants of reactions of nitroso oxides XC_6H_4NOO with methyl vinyl ketone in acetonitrile on the electronic properties of the substituent X in accordance with the Hammett equation.

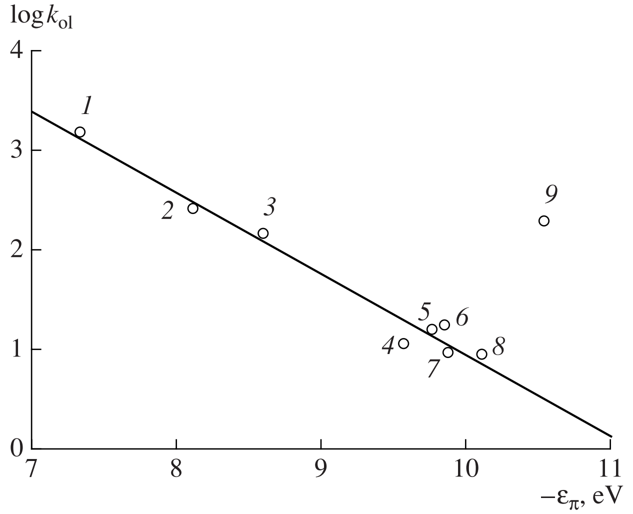

Fig. 5. Dependence of the rate constants of reactions of nitroso oxide **IIIa** with olefins in acetonitrile on the energy of a molecular orbital with a maximum contribution from the atomic orbitals of carbon atoms in the C=C bonds of the following olefins: (*1*) *trans*-stilbene, (*2*) styrene, (*3*) tetramethylethylene, (*4*) 1-hexene, (*5*) allylbenzene, (*6*) allyl alcohol, (*7*) allyl acetate, (*8*) allyl bromide, and (*9*) methyl vinyl ketone.

constants and the energies of molecular orbitals with the maximum contribution from the atomic orbitals of carbon atoms in the C=C bond ε_π. In terms of Koopmans' theorem, these energies taken with the opposite sign are equal to the corresponding ionization potentials. The value of ε_π for methyl vinyl ketone was 10.54 eV,[2] as calculated at the MP2/6-31G(*d*) level using the GAMESS program [16]. Figure 5 shows the dependence of the logarithms of the rate constants of reactions between nitroso oxide **IIIa** and olefins (k_{ol}) on the values of ε_π for the olefins [4] with the addition of the value for methyl vinyl ketone. This line does not contain the point corresponding to the latter value, which is noticeably larger than the rate constants of olefins with close ionization potentials.

Thus, methyl vinyl ketone cannot be placed in the same order with ordinary olefins because it is likely that the neighborhood of carbonyl and vinyl groups can affect the mechanism of 1,3-dipolar cycloaddition reactions of nitroso oxides to the C=C bond (Scheme 2). Because the molecule of methyl vinyl ketone has two possible reaction sites, it is likely that the reaction can occur at the carbonyl group. However, we studied the kinetics of decay of **IIIa** in acetone and obtained a rate constant of the same order of magnitude as that in acetonitrile [2]. Thus, it is most likely that the observed reaction of nitroso oxides with methyl vinyl ketone is the interaction with the C=C double bond. This problem can be clarified by studying the kinetics of the interaction of arylnitroso oxides with other α,β-unsaturated carbonyl compounds and analyzing the reaction products.

ACKNOWLEDGMENTS

This work was supported by the Russian Academy of Sciences (Department of Chemistry and Materials Science, program "Theoretical and Experimental Studies of the Nature of Chemical Bonds and Mechanisms of the Most Important Chemical Reactions and Processes") and by the Ministry of Education and Science of the Russian Federation (project no. RNP.2.2.1.1.6332, 2006–2008).

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[2] We are grateful to M.R. Talipov for calculating the ε_π value for methyl vinyl ketone.

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