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Chemically Induced Dynamic Nuclear Polarization During the Thermolysis of Alkoxyamines: A New Approach to Detect the Occurrence of H-Transfer Reactions

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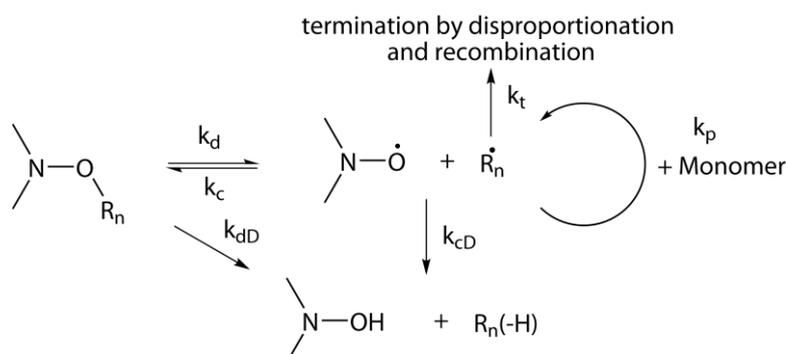
Abstract: Thermal decomposition of alkoxyamines in the presence of scavengers was found to proceed with the formation of chemically induced nuclear polarization detected by 1H NMR. The distinctive Chemically Induced Dynamic Nuclear Polarization (CIDNP) features were studied using the example of three alkoxyamines: 4-nitrophenyl 2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-2-methylpropanoate (**1a**), 4-nitrophenyl 2-(2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxy)-2-methylpropanoate (**2a**) and 4-nitrophenyl 2-(2,2,5,5-tetramethyl-4-phenyl-2H-imidazol-1-oxy)-2-methylpropanoate (**3a**) in the presence of PhSH. The analysis of CIDNP signs of methacrylate protons allows us to conclude on the occurrence of hydrogen atom transfer reaction in geminate radical pair formed in alkoxyamine thermolysis. Thus, CIDNP is a fast and sensitive method to detect the occurrence of intra/intermolecular hydrogen transfer in alkoxyamine thermolysis.

Keywords: nitroxide mediated polymerization; alkoxyamines; H-transfer reactions; CIDNP

1. Introduction

Nitroxide mediated polymerization (NMP) is a well established technique that allows for controlled growth of a polymer chain via the addition of persistent nitroxyl radicals. The method provides several features advantageous in polymer synthesis: the possibility to reinitiate polymer chain growth (so called “livingness”), the preparation of functionalized polymers, and the design of the architecture of copolymeric macromolecules [1–4]. The kinetic scheme for an ideal NMP reaction is the following (Scheme 1): reversible cleavage of alkoxyamines (so called “dormant” chain initiators) R_2NO-R_n into a propagating radical $R_n\cdot$ and a persistent nitroxyl radical $NO\cdot$, propagation, and irreversible termination. The theoretical background for this “ideal” mechanism and the optimal kinetic properties for the initiating alkoxyamine were presented previously by Fischer *et al.* [5,6], Fukuda *et al.* [7] and Solomon *et al.* [8] and showed that side reactions, in particular H-atom transfer, have a detrimental effect on the controlled regime of polymerization. Even a minor side reaction on alkoxyamine homolysis leads to incomplete monomer conversion and an increase in the final polydispersity of polymer.

Scheme 1. The mechanism of NMP with side reactions of H-atom transfer.



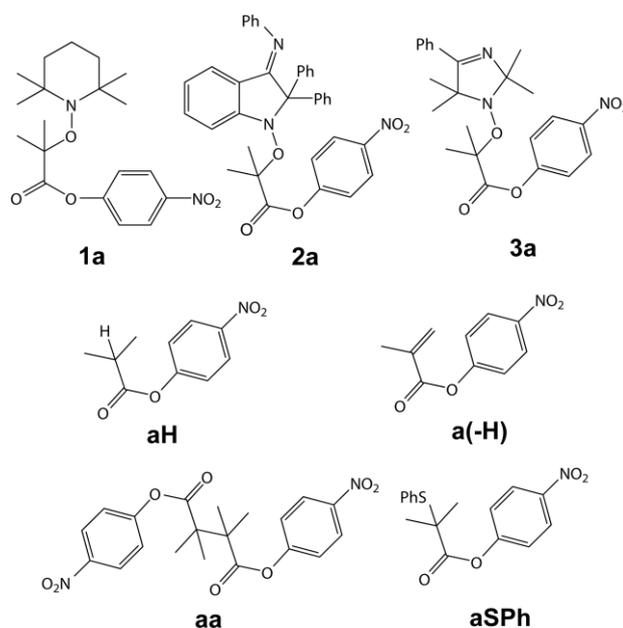
A comparative analysis of the H-transfer reaction between **1a** and **2a** (Chart 1) was performed recently [9]. The ^1H NMR analysis of the decomposition of alkoxyamines in the presence, and in the absence, of scavenger was performed. Such experiments provide information on the impact of intra/intermolecular H-transfer reaction on the decay of alkoxyamine. This approach was successfully applied to investigate the H-atom transfer reactions for a series of imidazoline, imidazolidine, and pyrrolidine-based alkoxyamines containing either isobutyrate-2-yl or 1-phenylethyl alkyl fragments [10].

In previous articles [9,10] we have reported the kinetics of thermolysis with long time delays between scans or at low temperatures where all NMR lines were nonpolarized. This article concerns the cases of high thermolysis temperature and short time delays when radical concentration is high enough to produce intensive Chemically Induced Dynamic Nuclear Polarization (CIDNP).

CIDNP effect arises from the spin selection process that occurs during a recombination reaction of radical pairs and leads to significant non-equilibrium electron and nuclear spin state populations, resulting in enhanced absorption and emission spectral lines, whose signs follow a set of well defined rules [11]. A molecule dissociates into two spin correlated radicals with the formation of a so called

geminate radical pair. The spin state of the geminate radical pair remains the same as that of the excited precursor molecule. For diffusive collision between two radicals one would expect a statistical distribution of spin states: $\frac{1}{4}$ in the singlet state ($S = 0$) and $\frac{3}{4}$ in the triplet state. CIDNP is widely applied for the determination of the multiplicity of intermediate RPs and their precursor excited molecules, identification of radical intermediates, determination of signs of hyperfine interaction (HFI) constants, study of reversible electron transfer reactions, *etc.* [11–14]. Previously, Chemically Induced Dynamic Electron Polarization (CIDEP) [15,16] and CIDNP and its modification (CIDNP with fast switching of magnetic field) have been used in NMP research to measure the rate constants of coupling between acrylate-type radicals and the persistent nitroxide [17,18]. In those experiments, the carbon centered radicals under investigation were generated by the photolysis of ketone precursors in the presence of persistent nitroxides. The coupling rate constants k_c were determined from the concentration dependence of observed CIDNP kinetics. Because the thermolysis of alkoxyamines involves formation of radical pairs consisting of nitroxyl and alkyl radicals (Scheme 1), CIDNP is expected to be observed on the products of thermolysis.

Chart 1. The structures of alkoxyamines and products of decomposition.



The measurement of NMR spectra during the decomposition of alkoxyamines **1a**, **2a**, [9] and **3a** [10], in the absence and in the presence of scavenger was previously performed. In this article we report the analysis of CIDNP signals observed during the decomposition of alkoxyamines **1a**, **2a**, and **3a** (Chart 1) in the presence of scavenger. The addition of scavenger leads to the strong CIDNP effects for the NMR lines of reaction products, whereas in the absence of scavenger CIDNP during the thermolysis of alkoxyamine was not observed. The CIDNP peculiarities at different experimental conditions were investigated and the CIDNP kinetics and CIDNP signs on nuclei belonging to different reaction products were analyzed. That is, different CIDNP signs were observed for the generation of alkene depending on the H-transfer processes: positive CIDNP signal for intermolecular H-transfer reactions occurring during the decomposition of alkoxyamine (geminate cage) or negative CIDNP signal for H-transfer reaction occurring during the disproportionation/dimerization of two alkyl radicals.

2. Experimental Section

Alkoxyamines were prepared as previously reported for **1a** [19], **2a** [20], **3a** [21]. Deuterated solvents and PhSH were purchased from Aldrich and used as received. 1,3-Dichloro-2,4,5,6-tetrafluorobenzene (Fsol) was received from Novosibirsk Institute of Organic Chemistry SB RAS. ^1H NMR experiments were performed on DRX-Avance-200 Bruker NMR spectrometer equipped with the BVT2000 temperature control unit. The kinetics of the alkoxyamine (Chart 1) thermolysis were measured for 0.02 M samples in d_6 -benzene, m-dichlorobenzene- d_4 or Fsol in the presence of excess (>3 equivalents) of thiophenol (PhSH) as radical scavenger. Samples were degassed by several freeze-pump-thaw cycles (10^{-3} mb) and sealed off under vacuum in conventional NMR tubes in order to avoid the formation of oxidation products. As previously reported, samples were placed into preheated probehead. NMR spectra were recorded with different time delays. Time intervals between measurements were chosen depending on typical timescale of kinetics aiming to observe the CIDNP signals. Fsol was used as high temperature boiling point (bp = 152 °C) solvent. As previously reported, PhSH was used as scavenger due to both its high reaction rate constants with alkyl and nitroxyl radicals, $k_2((\text{CH}_3)_3\text{C}\cdot) = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [22] and $k_1(\text{R}_1\text{R}_2\text{NO}\cdot) \approx 100 \text{ mol}^{-1} \text{ s}^{-1}$ [23], respectively, and its convenient ^1H NMR spectra. The signal of thiol proton of PhSH has chemical shift 3.02 ppm and does not overlap with any other NMR signals of alkoxyamines or of the products of its thermolysis.

3. Results and Discussion

3.1. Analysis of the Products of Thermolysis Reaction

The successful detection of CIDNP requires high NMR sensitivity. In particular the concentration of polarized molecule $[\text{M}^*]$ should not be less than $[\text{M}_{\text{min}}]$ —the minimum concentration of diamagnetic molecules which can be detected using NMR $[\text{M}_{\text{min}}] \sim 10^{-4} \text{ M}$. The concentration of polarized molecule is determined by the rate of its formation described by $\xi k_d[\text{A}]$ (with ξ the coefficients describing the efficiency of CIDNP formation of geminate radical pair formed from thermally excited singlet molecule $[\text{A}]$, k_d the decomposition rate constant, and $[\text{A}]$ the alkoxyamine concentration) and the rate of polarization decay due to nuclear spin relaxation with the rate $1/T_1$ (T_1 the nuclear relaxation time). At initial time of thermolysis ($[\text{A}] = [\text{A}]_0$) we can roughly evaluate $[\text{M}^*] \sim k_d[\text{A}]_0 T_1 \xi$. Thus for CIDNP observation the rate of alkoxyamine decay should be higher than $k_d[\text{A}]_0 > [\text{M}_{\text{min}}]/T_1 \xi$. Taking into account nuclear relaxation time of CH_3 group protons of alkoxyamine as $T_1 \sim 1 \text{ s}$ and typical CIDNP enhancement factor as 10^2 – 10^3 , we can conclude that the rate of alkoxyamine decay should be higher than 10^{-6} M s^{-1} , that is, $k_d > 5 \cdot 10^{-5} \text{ s}^{-1}$ for initial alkoxyamine concentration $[\text{A}]_0 = 20 \text{ mM}$ (our typical experimental conditions). Taking into account that the typical life time of alkyl radicals during thermolysis ($1/k_d$) is shorter than nuclear relaxation time of alkyl radical 10^{-4} – 10^{-5} s^{-1} , relaxation processes could be a factor decreasing polarization of escape radicals.

The CIDNP pattern strongly depends on the time of observation, the temperature of thermolysis and thiophenol concentration. The CIDNP intensity was very weak during homolysis at temperatures below 70 °C when the experiment was performed in C_6D_6 , but was nicely observed at higher temperatures during experiments in Fsol (Figure 1). Note that at temperatures above 70 °C, the

amount of generated radicals was high, thus, the requirement for the minimum concentration of polarized molecules was fulfilled and CIDNP was detected. In the absence of scavenger, CIDNP was not observed at all (temperatures 110–70 °C) due to the reversibility of alkoxyamine decay (about 97% for **1a** taking into account H-atom transfer) [9,24] leading to cancellation of in-cage and escape products. Since a reversible reaction has no net chemical change, no polarization would be expected to be observed since geminate recombination of the radical pair leads to one polarization and the escaping radicals carry the opposite polarization, canceling out the whole effect. Indeed, as one can see from Scheme 2, CIDNP on alkoxyamine is formed via two ways—geminate recombination of the radical pair leads to positive polarization (Reaction 1) and the escaping radicals carry the negative polarization (Reaction 3), canceling out CIDNP effect. Side reaction or nuclear relaxation time in the intermediate radicals in the absence of scavenger could play the same role and make CIDNP visible. Evaluation shows that the lifetime of alkyl radical is much less than nuclear spin relaxation time and could not explain CIDNP formation. Due to persistent radical effect [5] in the absence of scavenger the concentration of nitroxide is more than several orders of magnitude higher than the same of free radicals. The rate of Reactions 6 and 7 is much smaller in comparison with Reaction 3 and CIDNP formation due to these reactions is negligible.

Scheme 2. The kinetic scheme of decomposition of alkoxyamine in the presence of thiophenol. Letters in brackets indicate the sign of CIDNP: *A*—absorption, *E*—emission.

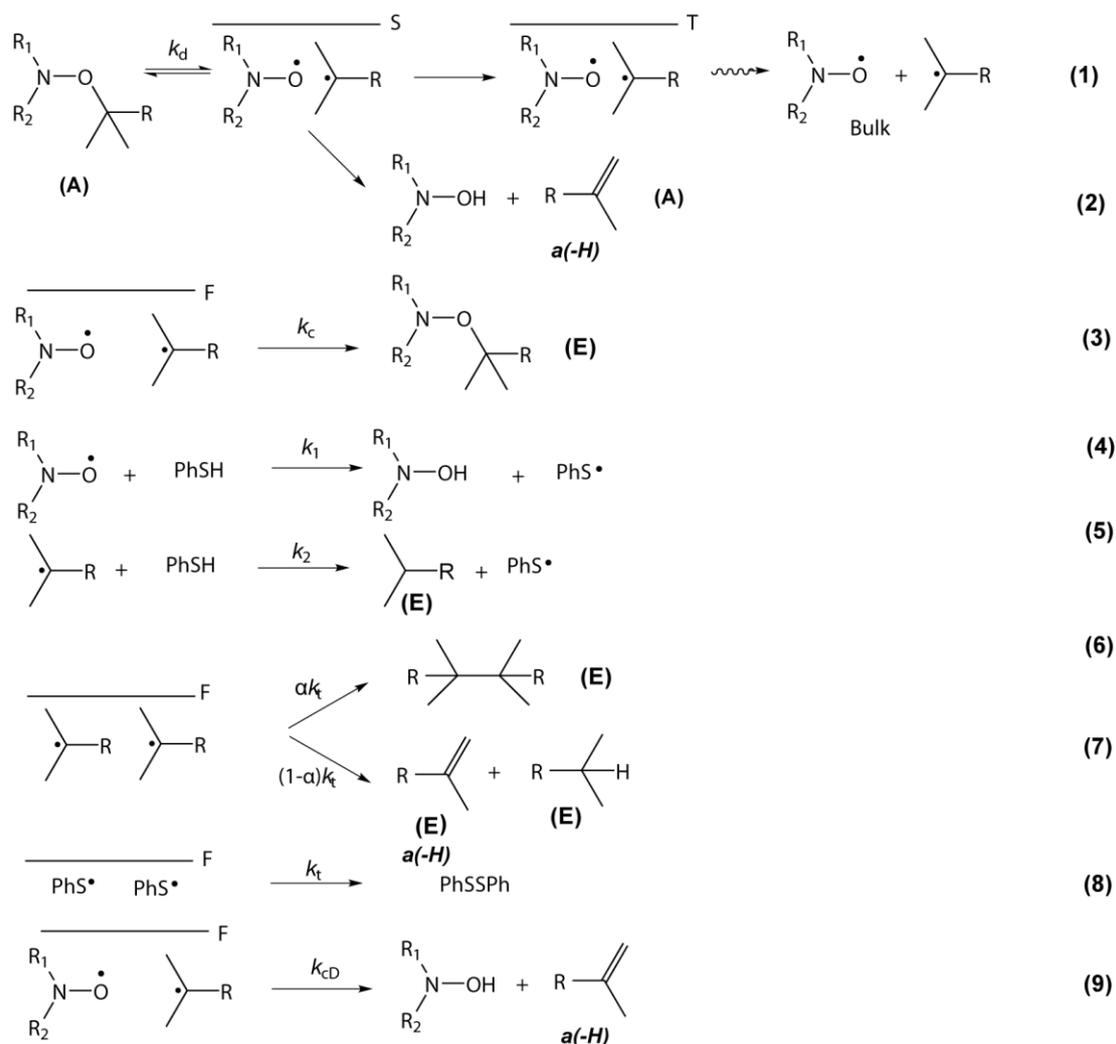
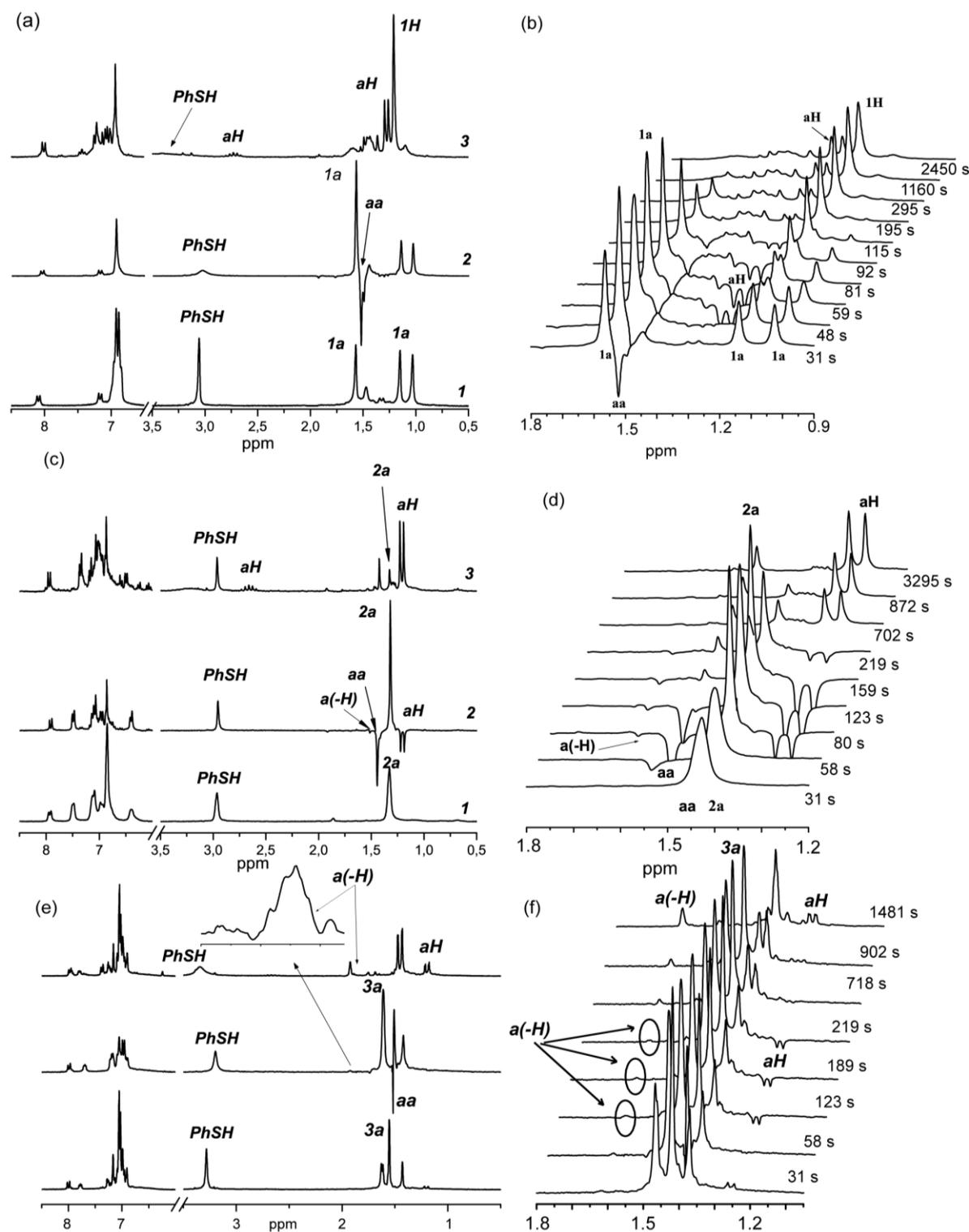


Figure 1. ^1H NMR spectra recorded at room temperature before (1) and after (3) thermolysis of **1a** (a), **2a** (c) in FSol and **3a** (e) in $m\text{-C}_6\text{D}_4\text{Cl}_2$ and spectra with polarized signals obtained during the thermolysis (2). ^1H NMR spectra recorded at different time intervals from the beginning of the reaction during thermolysis of **1a** (b) at 398 K, 0.02 M solution of alkoxyamine in FSol, 5.5 eq of thiophenol, **2a** (d) at 386 K, 0.02 M solution of alkoxyamine in FSol, 3 eq of thiophenol, **3a** (f) at 386 K, 0.02 M solution of alkoxyamine in $m\text{-C}_6\text{D}_4\text{Cl}_2$, 6 eq of thiophenol. Signs of polarization: E — aa , $a(-H)$, aH ; A —**1a**–**3a**. Inset: enlargement of the chemical shift zone for $a(-H)$ of **3a**.



In the presence of radical scavenger, alkoxyamine is formed only as in-cage product of geminate radical pair RP, whereas escape radicals react with PhSH with the formation of alkane **aH**, hydroxylamine and other compounds. Thus, in this case CIDNP intensity of alkoxyamine is equal to the overall intensity of CIDNP of escape products, but with the opposite sign.

According to Kaptein's rules [25], the sign of CIDNP net effect (Γ) is determined by the initial spin multiplicity of intermediate RP (μ), the sign of HFI constants (A_{HFI}), the sign of the difference in g -factors of radical partners, and the way of product formation (ε) (in-cage or out-cage).

$$\Gamma = \mu \cdot \varepsilon \cdot \Delta g \cdot A_{HFI} \quad (1)$$

These parameters for the radical pair under investigation are the following: $a(\text{CH}_3) > 0$, g -factor of intermediate radicals are $g = 2.0027$ for tertiary alkyl radical [26] and $g = 2.0059$ for nitroxyl radical [27,28], thus $\Delta g < 0$, and $\varepsilon = 1$ for alkoxyamine which is in-cage product, or $\varepsilon = -1$ for other escape products (**aa**, **aH**, etc.). Thus, as it follows from Equation (1), CIDNP is formed in the geminate *singlet* RP ($\mu = -1$) but not in diffusion RP ($\mu = 1$). The kinetic scheme of decomposition of alkoxyamine in the presence of thiophenol is shown in Scheme 2. The multiplicity of radical pairs in Scheme 2 is denoted as S- for singlet RPs, T- for triplet RPs and F- for diffusion RPs. The expected signs of CIDNP of reaction products emission (E) or absorption (A) are indicated in Scheme 2. It should be noted that CIDNP effect on the protons of **aa** is originated from geminate RP only but not from diffusion RPs, because in high magnetic fields CIDNP in radical pairs of two similar radicals is equal to zero [11].

NMR spectra before, during and after thermolysis of alkoxyamine **1a–3a** in the presence of PhSH are shown in Figure 1. CIDNP is observed on NMR lines of alkoxyamines (**1a**, **2a**, **3a**) and several reaction products of alkoxyamine decomposition in the presence of thiophenol, *i.e.* dimer of two alkyl radicals (**aa**), product of reaction of alkyl radicals with PhSH (**aH**), and alkene product **a(-H)**.

The compound **a(-H)** can be formed in three different reactions (*i*) as a disproportionation product of two alkyl radicals (emissive CIDNP signal, Equation 7, Scheme 2), (*ii*) as a product of hydrogen transfer from alkyl to nitroxide radical in the geminate RP (absorption CIDNP signal, Equation 2, Scheme 2) and in the diffusion RP (at the very early stage without CIDNP signal, Equation 9, Scheme 2), and (*iii*) as a product of intramolecular proton transfer (no CIDNP signal, k_{dD} in Scheme 1). In the case of **1a** thermolysis the signal of **a(-H)** overlaps with much higher intensity signal of alkoxyamine **1a** thus no conclusion about its CIDNP sign can be made. The observed CIDNP intensity of **a(-H)** protons was very weak and was negative in the case of **2a** thermolysis, and positive in the case of **3a** thermolysis. CIDNP on the protons of **a(-H)** can be formed in two ways: negative polarization is formed after recombination of two escape alkyl radicals (Equation 7, Scheme 2), or positive polarization is formed in the case of hydrogen atom transfer in geminate RP. The negative CIDNP signal for **a(-H)** during decomposition of **2a** in the presence of scavenger was detected pointing at the reaction of two alkyl radicals and confirming the non-occurrence of intermolecular H-transfer for **2a**. For **3a** the intermolecular H-transfer reaction has a large contribution to the decomposition kinetics, so that the sign of polarization on **a(-H)** is positive. Note that CIDNP intensity of NMR line of CH_3 group of **a(-H)** is substantially lower than the same for **aa**. Fischer and co-authors [29] have studied coupling (Reaction 6, Scheme 2) and disproportionation (Reaction 7, Scheme 2) and showed that the ratio between recombination and disproportionation products yields depends on

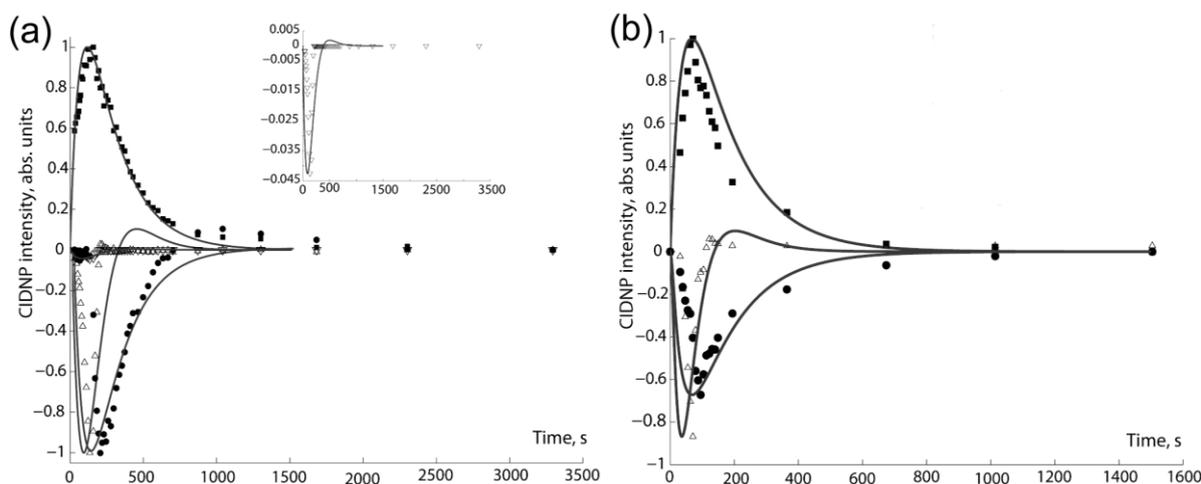
temperature. For $T = 100\text{ }^{\circ}\text{C}$ this ratio is $\sim 1/5$. In addition, the number of protons contributing to NMR lines of CH_3 groups of **aa** is equal to 12 and while that for **a(-H)** it is equal to 3. Thus, the expected difference in CIDNP intensity of CH_3 groups of **aa** and **a(-H)** is about 20-times and is in a good agreement with the experimental ratio of 23.

Consequently, the sign of polarization on **a(-H)** provides valuable information on the main process that contributes to its formation: for experiment with **2a** alkene **a(-H)** is issued from Reaction 7 (Scheme 2), whereas for **3a** decomposition alkene is the product of H-atom transfer reaction (Equations 2 and 9 at the very early stages, Scheme 2).

3.2. Kinetics of CIDNP

Figure 2 shows CIDNP kinetics obtained using NMR lines of different products during thermolysis of **2a**. As expected, CIDNP intensity of **2a** slightly exceeds the CIDNP intensity of escape products. Typical CIDNP kinetics consists of two parts (Figure 1 and Figure 2), rise and decay, and can be described by two exponent functions.

Figure 2. Kinetics of polarized signals (normalized) during thermolysis of 0.02 M solution of alkoxyamines in FSol **2a** (a) at 386 K in the presence of 3 eq. of thiophenol and **3a** (a) at 386 K in $m\text{-C}_6\text{D}_4\text{Cl}_2$ in the presence of 6 eq of thiophenol: (■)—alkoxyamine **2a**, (●)—alkane **aH**, (Δ)—dimer **aa**, (∇)—alkene **a(-H)**. (b): (■)—alkoxyamine **3a**, (●)—alkane **aH**, (Δ)—dimer **aa**. Inset—the kinetics of CIDNP on **a(-H)** for **2a**. Inset: enlargement of evolution of CIDNP signal for **a(-H)**—(∇) of **2a**. Solid line—calculated dependence of CIDNP vs. time.



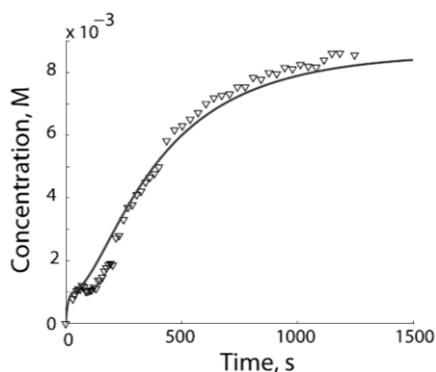
An increase of CIDNP intensity on alkoxyamine is observed at time intervals of less than 200 seconds. The emission signal on **aa** is observed at even shorter time intervals (typically 100 s) in Figure 1b and d. During this time the concentration of alkyl radicals is high enough to favor the reactions 6 and 7 (Scheme 2) and recombination of alkyl radical with nitroxide, *i.e.*

$$k_t[R], k_c[NO\bullet] \geq k_{PhSH} [PhSH] \quad (10)$$

Time evolution of CIDNP on the protons of **aa** is much faster than the same for alkoxyamine and alkane **aH**. The kinetic profile of CIDNP on **aH** is the same as for alkoxyamines **1a**, and **2a** which

highlights that alkane **aH** is mainly issued from the reaction of alkyl radicals with thiophenol. CIDNP kinetics of **a(-H)** and **aa** (Figure 2) during the decomposition of **2a** exhibits the same time profile confirming that these two species are formed in the same reaction of alkyl radicals which is important at the earliest stage of thermolysis. The emissive polarization on **a(-H)** (Figure 2a inset) indicates that alkene is mainly formed in alkyl-alkyl radicals reaction confirming the very low level of H-transfer reaction in nitroxyl-alkyl geminate RP of **2a** as concentrations as low as 10^{-6} M of species can be detected. Meaning that fraction of ca. 0.01% of intermolecular H-transfer in alkoxyamine might be detected in our experimental conditions. Consequently, as H-transfer reactions exhibit detrimental effect for fraction larger than ca. 0.5%, sensitivity of CIDNP is a valuable tool for screening the occurrence of H-transfer reaction in alkoxyamine.

Figure 3. Kinetics of polarized NMR line of alkene **a(-H)** during thermolysis of 0.02 M solution of **3a** (b) in $m\text{-C}_6\text{D}_4\text{Cl}_2$ at 386 K in the presence of 6 eq of thiophenol: symbols—experimental data points, solid lines—calculated dependence vs. time.



Contrary to **2a**, alkoxyamine **3a** exhibits high fraction of H-atom transfer (at 95 °C, 30% and 15% for intramolecular proton transfer and intermolecular H-transfer reactions, respectively) [10]. Thus, as mentioned above, one would expect positive polarization on **a(-H)**. Unfortunately there is no unpolarized line for **a(-H)** product, so that the CIDNP kinetics cannot be extracted and, thus, the evolution of NMR signal of polarized CH_3 protons of alkene which is the sum of CIDNP and steady state NMR signal of alkene is displayed in Figure 3. However, the growth of **a(-H)** is well described by the proposed model (*vide infra*) as well as the break in the growth of signal which is due to the overlapping between the CIDNP signal and the steady state NMR signal of alkene. This indicates that the main pathway of alkene formation is H-atom transfer reaction in geminate RPs.

The kinetics of the concentration and CIDNP of alkoxyamine are described by the following equations:

$$\frac{d[A]}{dt} = -(k_d + k_{dB})[A] + k_c[N][R] \quad (11)$$

$$\frac{dP^A}{dt} = -k_d\xi[A] + k_c\chi[R][N] - \frac{P^A}{T_1} \quad (12)$$

where $[A]$, $[N]$, $[R]$ are the concentrations of alkoxyamine, nitroxide and alkyl radical, respectively, and P^A and P^R are the nuclear polarization of alkoxyamine and alkyl radical; ξ and χ are the coefficients describing the efficiency of CIDNP formation of geminate radical pair formed from

singlet precursor and diffusion radical pair of nitroxide and alkyl radical and $1/T_1$ is nuclear relaxation time. ξ and χ depend on hyperfine constants of radical partners, difference in g-factors, and radical pair lifetime, which is determined by mutual diffusion coefficient, reaction radius and recombination rate constant [11].

Let us consider the case of high PhSH concentration. In this case the recombination rate of radicals in the bulk (Reactions (3), (6), (7) and (9), Scheme 2) is negligible in comparison with the reaction rate of radicals with PhSH (Reaction (5), Scheme 2). When condition $k_t[R][R], k_c[N][R] \ll k_{PhSH}[PhSH][R]$ is valid, alkoxyamine is formed predominately as in-cage product of geminate radical pair while alkyl radical escaping from geminate radical pair into the bulk are scavenged by PhSH giving alkane RH. The concentration of alkoxyamine under this condition is described by monoexponential decay with the rate constant equal to k_d (Equation 14). The formation of alkoxyamine polarization in diffusion radical pairs of alkyl and nitroxyl radicals (Reaction 3, Scheme 2) in the bulk (second term in Equation 12) can be neglected and the polarization of alkoxyamine P^A is described by Equation 13. With taking into account initial condition (polarization at $t = 0$ is equal to zero), it is easy to obtain the analytical expression for the polarization of alkoxyamine P^A Equation (15) combining the Equations (13) and (14):

$$\frac{dP^A}{dt} = \xi k_d [A] - \frac{P^A}{T_1} \quad (13)$$

$$[A](t) = [A]_0 e^{-(k_d + k_{dD})t} \quad (14)$$

$$P^A(t) = [A]_0 \xi \frac{k_d}{k_d + k_{dD} - 1/T_1} (e^{-t/T_1} - e^{-(k_d + k_{dD})t}) \quad (15)$$

Thus, the concentration of polarized molecules is determined by two exponents with parameters k_d , k_{dD} and $1/T_1$. At short times $t \ll 1/k_d$ it grows with typical rise time T_1 and at longer times $t > 1/T_1$ it decays with parameter $k_d + k_{dD}$. The intensity of polarization is determined by CIDNP enhancement factor, nuclear relaxation time and decay rate constant. The expected time of CIDNP maximum obtained from expressions (13–15) is equal to:

$$t_{\max} = \frac{\ln((k_d + k_{dD})T_1)}{k_d + k_{dD} - 1/T_1} \quad (16)$$

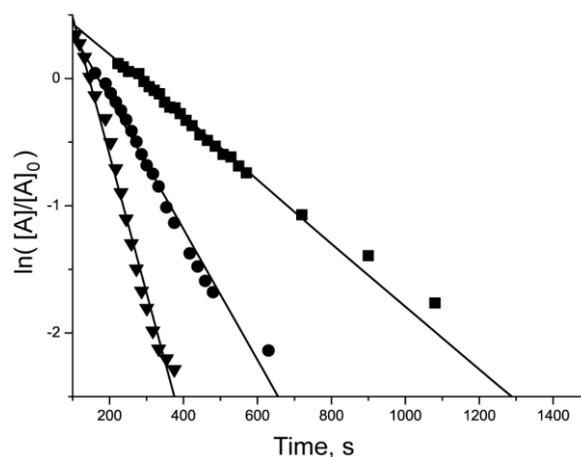
Substitution of k_d and T_1 gives much shorter time (several seconds) than experimentally observed. Although the NMR tube was placed into preheated NMR probe, the heating of the sample to the aimed temperature took 1–2 minutes and was different for different temperatures [30].

In order to confirm the mechanism of formation of polarization the kinetic scheme of alkoxyamine thermolysis in the presence of scavenger was solved numerically (for the reactions see Scheme 2, the equations are presented as SI). The resulting polarization dependences are presented in Figure 2a and b (solid lines). The values of rate constants are the following: $k_d = 0.003 \text{ s}^{-1}$ for **2a** and $k_d = 0.007 \text{ s}^{-1}$ for **3a**, [9] $k_c = 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for **2a**, [31] $k_c = 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for **3a**, [19,32] $k_t = 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_1 = 100 \text{ M}^{-1} \text{ s}^{-1}$, [23] $k_2 = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, [22], $[A]_0 = 0.02 \text{ M}$, $[PhSH]_0 = 0.06 \text{ M}$, $T_1 = 1 \text{ s}$, $P = 100$. The values of nuclear spin relaxation time of products were measured for every NMR line in the spectrum. The numerical decay of CIDNP polarization agrees with experimental data (Figure 2). As

follows from the numerical calculations, the second part of the CIDNP kinetics of alkane **aH** is fully governed by the decomposition of alkoxyamine. The kinetics of **aa** formation are much faster as two processes contribute to the formation of polarization on **aa**: (i) polarization formed in bulk singlet radical pair which is emissive and (ii) polarization in the triplet radical pair which gives absorption. The resulting evolution of CIDNP on **aa** exhibits very sharp decay and growth. In the case of **2a** the alkene **a(-H)** is formed in the same reactions as dimer **aa** the kinetics of CIDNP is due to similar processes, although due to low signal intensity not all peculiarities can be seen on it (Figure 2a inset). The main contribution to the polarization on alkene during decomposition of **3a** is H-atom transfer reaction in geminate RP. Thus the calculation confirmed that positive polarization should be observed in this case. As mentioned above there is no non-polarized lines for alkene in the spectra. The non-polarized signals of the protons of the ring of *p*-Ph-NO₂ group overlap with the signals of PhSH. Thus to achieve agreement, the experimental data were simulated with the sum of concentration and polarization functions. The resulting calculated curve is in a good agreement with the experimental dependence of polarization on alkene.

The increase of polarization is fully governed by the value of nuclear spin relaxation time. For the values measured for alkoxyamine **1a** and alkane **aH** ($T_1 = 1$ s) the maximum of the polarization kinetics on alkoxyamine should be observed at $t < 10$ s. When the calculated function of alkoxyamine CIDNP kinetics is multiplied by the experimental curve of sample heating up in the probe head of NMR spectrometer, good enough agreement with the experimental data is observed. Thus, in our case the growth of the alkoxyamine CIDNP kinetics is governed by the heating process assuming the heating-up function is exponential. The parameter of exponent was determined experimentally in each case.

Figure 4. Kinetics of CIDNP on alkoxyamine **1a** during thermolysis of 0.02 M solution of alkoxyamine in FSol in the presence of thiophenol and its fit (line) with monoexponent in semi-logarithmic scale: 361 K, [PhSH] = 0.1 M (■), 373 K, [PhSH] = 0.136 M (●), 398 K, [PhSH] = 0.13 M (▼). The values of k_{obs} obtained from the fit: 361 K— $k_{\text{obs}} = 2.0 \times 10^{-3} \text{ s}^{-1}$, 373 K— $k_{\text{obs}} = 5.0 \times 10^{-3} \text{ s}^{-1}$, 398 K— $k_{\text{obs}} = 1.5 \times 10^{-2} \text{ s}^{-1}$.



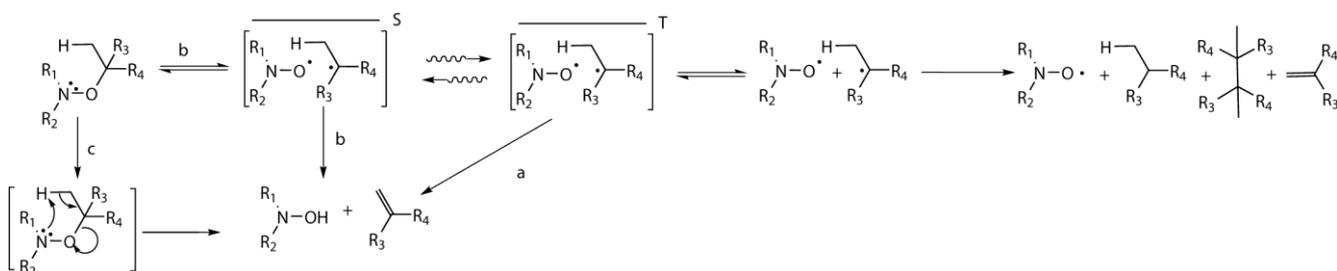
At time longer than 200 seconds, CIDNP kinetics are detected only on the protons of alkoxyamines and **aH**. The CIDNP kinetics decays of **1a–3a** at $t > 200$ s were described by monoexponential function with the decay parameter equal to $k_{\text{obs}}(T)$. As an example Figure 4 shows CIDNP kinetics in logarithmic scale for **1a** providing k_{obs} of $2.0 \times 10^{-3} \text{ s}^{-1}$, $5.0 \times 10^{-3} \text{ s}^{-1}$, and $1.5 \times 10^{-2} \text{ s}^{-1}$

at 361 K, 373 K, and 398 K, respectively. Within experimental error k_{obs} coincide with k_d reported using unpolarized NMR signals of alkoxyamines or EPR [9,10]. Consequently, the presence of CIDNP effect does not impede the determination of k_d .

4. Conclusions

In this work we report the first observation of ^1H CIDNP during decomposition of alkoxyamines in the presence of effective alkyl radical scavenger. The analysis of the polarization kinetics can give an insight to the mechanism of side reactions during homolysis. Using the polarized signal of alkene product, the absence of H-atom transfer reaction for alkoxyamine **2a** based on nitroxide 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxy and its presence for imidazolidine-based alkoxyamine were confirmed. Thus, alkene can be generated during the decomposition of alkoxyamine through three pathways: two radical pathways, *i.e.*, intermolecular H-transfer occurring both in the diffusion RP during the re-formation of alkoxyamine (Route a, Scheme 3) [33] and in the geminate RP during the thermolysis (Route b, Scheme 3); and a non-radical pathway, *i.e.*, intramolecular proton transfer (Cope-type elimination, Route c, Scheme 3) occurring during the thermolysis of alkoxyamine.

Scheme 3. The different pathways affording the generation of alkene during the decomposition/reformation of alkoxyamine.



Hence, providing that the kinetic and concentration requirements are fulfilled and the resolution adequate, CIDNP technique is a valuable tool to detect H-transfer reaction in alkoxyamine and, hence, to probe quickly the potential of an alkoxyamine as initiator and controller for NMP.

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