H-Transfer Reaction During Decomposition of *N*-(2-Methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1)-Based Alkoxyamines

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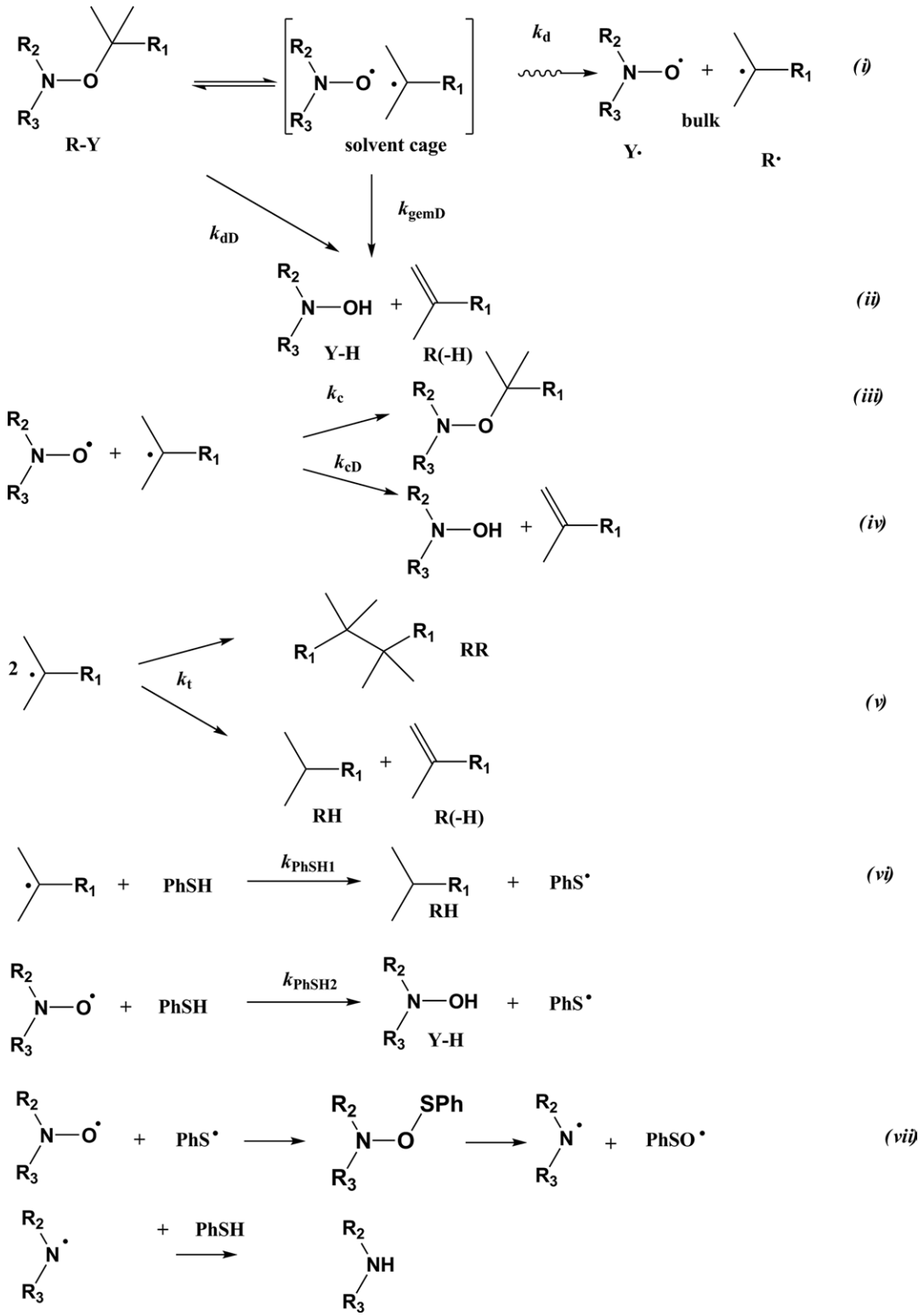
ABSTRACT: Thermal decomposition of four tertiary *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1)-based alkoxyamines (SG1-C(Me)$_2$-C(O)-OR, R = Me, tBu, Et, H) has been studied at different experimental conditions using ^{1}H and ^{31}P NMR spectroscopies. This experiment represents the initiating step of methyl methacrylate polymerization. It has been shown that H-transfer reaction occurs during the decomposition of three alkoxyamines in highly degassed solution, whereas no products of H-transfer are detected during decomposition of SG1-MAMA alkoxyamine. The value of the rate constant of H-transfer for alkoxyamines **1** (SG1-C(Me)$_2$-C(O)-OMe) and **2** (SG1-C(Me)$_2$-C(O)-OtBu) has been estimated as 1.7×10^3 $M^{-1}s^{-1}$. The high influence of oxygen on decomposition mechanism is found. In particular, in poorly degassed solutions, nearly quantitative formation of oxidation product has been observed, whereas at residual pressure of 10^{-5} mbar, the main products originate from H-atom transfer reaction. The acidity of the reaction medium affects the decomposition mechanism suppressing the H-atom transfer. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: initiators; kinetics (polym.); living polymerization; radical polymerization; reactive processing

INTRODUCTION Nitroxide-mediated polymerization (NMP) discovered in the mid-80s by Rizzardo and coworkers[1] opens an easy and convenient way to well-defined, end-functionalized, low-polydispersity polymeric materials.[2–6] The kinetic scheme of NMP is based on the conventional kinetic scheme of radical polymerization: (i) initiation stage including homolysis and reformation of the initiating alkoxyamine (k_d and k_c, respectively) and the addition of the initiating alkyl radical onto monomer (k_{add}), (ii) the propagation stage including the homolysis and the reformation of the macroalkoxyamine (dormant species, $k_{d,ds}$ and $k_{c,ds}$, respectively) and the propagation of the polymeric chain (k_p), and (iii) the termination stage including the self-termination reactions (disproportionation and dimerization reactions) and the reaction between alkyl and nitroxyl radicals (Supporting Information Scheme 1).The level of self-termination reactions is usually low in NMP, which makes the preparation of controlled and living polymers possible.[2,6,7]

The first effective NMP was carried out for styrene in the presence of commercially available nitroxide TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) by Georges coworkers.[7] Afterward many new nitroxides were developed as the mediating agents for NMP.[8] One of the most effective NMP mediators of many styrenic and acrylic monomers is the *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl radical (SG1).[9] Up to date, NMP of alkyl methacrylates, in particular methyl methacrylate (MMA), is very demanding, although a number of attempts using different nitroxides or alkoxyamines have been performed.[10–19] The main complication for NMP of MMA is the occurrence of side reactions, namely, the intramolecular β-proton transfer (IPT, Cope-type elimination[20]), intermolecular β-hydrogen atom transfer (IHAT) reactions (reactions (ii) and (iv), respectively, in Scheme 1), irreversible decomposition of dormant species (i.e., through NO bond homolysis),[21–23] and decomposition of persistent nitroxyl radicals in the course of NMP.

Additional Supporting Information may be found in the online version of this article.



SCHEME 1 Reaction scheme for decomposition of alkoxyamine (R-Y) at different conditions.

Although Fischer's diagram approach[24] predicts good control of MMA polymerization initiated by *N*-(2-methylpropyl)-*N*-(1-diethylposphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl) hydroxylamine (SG1-MAMA), it could not be reached in experiment.[25] The possible reasons of unsuccessful NMP using SG1-MAMA have been intensively discussed in literature. On the one side, Ananchenko et al.[26] concluded that impact of H-transfer reaction is insignificant during the

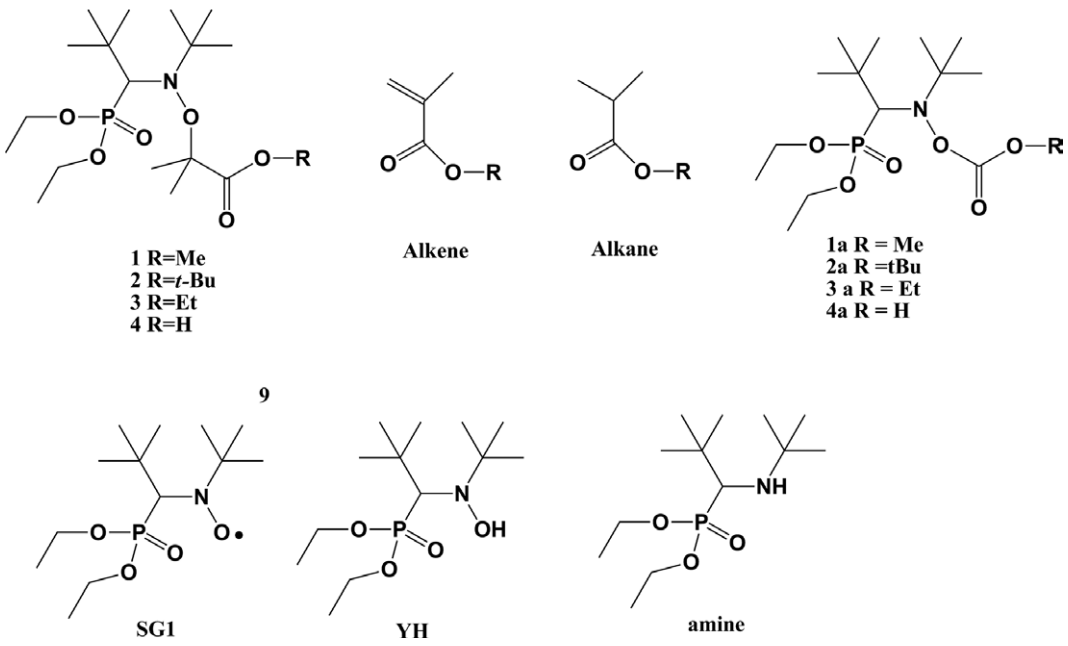


FIGURE 1 Alkoxyamines under investigation and products of reactions.

homolysis of SG1-based alkoxyamines. On the other hand, McHale et al.[27] showed that the large excess of free SG1 in the reaction medium can stimulate the occurrence of H-transfer. The numerical simulation of the IHAT between SG1 and the poly(methylmethacrylyl) radical performed by Dire et al.[28] leads to conclusion that the large excess of SG1 promotes the H-atom transfer reaction with the k_{cD} values of 1.7×10^3 $M^{-1}s^{-1}$. Guillaneuf et al.[25] noted that the penultimate and chain length effect arising from both sterically hindered nitroxide (SG1) and macro radical lead to an excessively large equilibrium constant K, which in combination with even low-level intermolecular H-transfer ($k_{cD}/k_c \approx 0.1\%$) makes the control of polymerization impossible. The real breakthrough was made by Charleux et al.[29,30] who have shown that copolymerization of MMA is possible at moderate temperature (80–90 °C) with high conversion and high livingness in the presence of small amount of styrene and additional free SG1.

In this article, we report the detailed analysis of initiating step of MMA polymerization mediated by SG1. The mechanism of thermal decomposition of four SG1-based alkoxyamines (Fig. 1) has been investigated using the experimental approach developed and successfully applied by us previously.[22,23] In particular, for exhaustive study of processes occurring during decomposition of SG1-based alkoxyamines we have analyzed the reaction products and kinetics using ^1H and ^{31}P NMR spectroscopy at different experimental conditions: (i) in the presence or in the absence of scavenger, (ii) in acidic or nonacidic conditions, and (iii) in the presence or absence of oxygen. Based on the results obtained, complete decomposition mechanism has been proposed and kinetics of alkoxyamines decomposition simulated. It has been shown that in highly degassed solution IHAT occurs during the decomposition of alkoxyamines **1–3**, whereas no products of H-transfer are detected during the decomposition of **4**. On the other hand, a side-product of alkoxyamine type **1a** is formed in the presence of oxygen, which is confirmed by numerical kinetic simulations accounting for the hydrogen transfer. The obtained k_{cD} value for IHAT during the homolysis of alkoxyamine **1** is very close to that found for the macroalkoxyamine by Dire et al.[28]

EXPERIMENTAL

General

Alkoxyamines **1–3** were synthesized according to procedure described previously[31] using a reaction of SG1 radical with corresponding alkyl bromides. Alkoxyamine **4** and nitroxide SG1 were provided by Arkema. SG1 nitroxide was purified by column chromatography (SiO_2, pentane-ethylacetate gradient elution, 97% purity by ^1H NMR after reduction). All deuterated reagents, solvents, and thiophenol were purchased from Aldrich and used as received.

Kinetic Experiments

Kinetic experiments were performed using Bruker Avance 200 NMR spectrometer equipped with the BVT-2000 temperature unit. A typical alkoxyamine, hydroxylamine, or nitroxide decomposition experiment was carried out as follows: the alkoxyamine solution (20 mM) in benzene-d_6 or 1,2-dichlorobenzene-d_4 was placed in a conventional NMR tube with an excess (7–12 equiv.) of scavenger thiophenol (PhSH). The sample was degassed by three freeze-pump-thaw cycles (10^{-3} mbar) using oil pump or by five freeze-pump-thaw cycles (10^{-5} mbar) using high-vacuum pump, sealed under vacuum, and then placed into the preheated probehead of the NMR spectrometer. ^1H NMR spectra versus time were

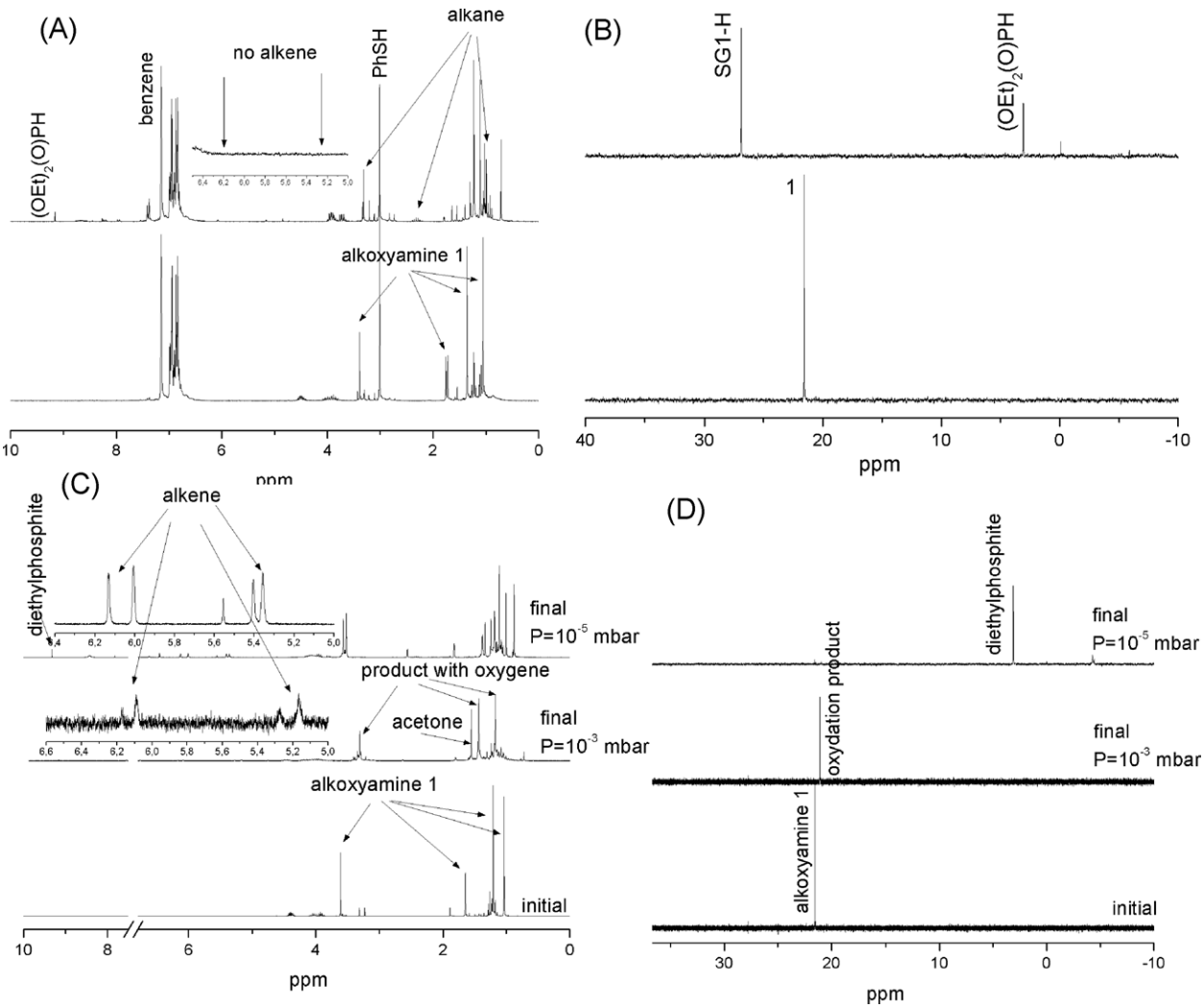


FIGURE 2 ^{1}H NMR (a,c) and ^{31}P NMR (b,d) detected before (lower) and after decomposition of alkoxyamine **1** (0.02 M solution in benzene, d_6) in the presence (a,b) and absence (c,d) of 0.2 M of PhSH. $T = 75$ °C.[39,40] Values of pressure are shown in the plots.

recorded during alkoxyamine decomposition at a given temperature. ^{1}H and ^{31}P NMR spectra were recorded at room temperature before and after kinetic experiment. PhSH, which is the scavenger of alkyl radicals and reducing agent of nitroxides, has the high reaction rate constants with alkyl and nitroxyl radicals:[32,33] $k_{PhSH}((CH_3)_3C\bullet) = 2.5\ 10^8\ M^{-1}s^{-1}$ and $k_{PhSH}(R_1R_2NO\bullet) \approx 100\ M^{-1}s^{-1}$, respectively. It should be mentioned that the reaction mechanism of thiophenol with nitroxides is rather complicated and is not shown on Scheme 1 in details. In particular, formed PhS· radical can react with nitroxides with formation of amines and other products.[34–36] Although it does not affect the alkoxyamine decomposition mechanism and kinetics, thiophenol reacts rapidly with alkyl radicals (reaction vii, Scheme 1) suppressing the back recombination. The S*H* proton signal (3.1 ppm) does not overlap with the vinylic or alkyl ^{1}H signals of alkoxyamines or the thermolysis products. The kinetics of alkoxyamine decomposition was obtained by automatic integration of the NMR signals of the alkoxyamines. The value of k_d was found by linear fitting of the decomposition kinetics in semilogarithmic coordinates.

Identification of Decomposition Products of Alkoxyamine 3

Decomposition Products of 3 after Degassing at Low Pressure (10^{-3} mbar) in tert-BuOH or $CDCl_3$ at 70 °C

The main product observed was **3a** as identified by ^{1}H and ^{31}P NMR and MS analyses: ^{1}H NMR (300 MHz): 1.13 (9H, s), 1.20 (9H, s), 1.26–1.34 (9H, m), 3.26 (1H, d, 24 Hz), 4.06–4.27 (6H, m), ^{31}P NMR 24.7, $M = 368.2198$ ($M+H^+$, theor368.2197), 86%. The typical signal of acetone was also observed by ^{1}H NMR ($\delta = 1.55$ ppm). The 14% left were simple phosphates (^{31}P NMR δ (ppm): 9.73, 3.79–2.58), and mainly diethyl phosphite $(EtO)_2P(O)H$ ($\delta = 3.03$ ppm).

Decomposition Products of 3 after Degassing at High Pressure (10^{-5} mbar) in tert-BuOH or $CDCl_3$ at 70 °C

The main product observed were the diethylphosphite as identified by ^{31}P NMR ($\delta = 3.03$ ppm, 85%), and 15% of **3a** ($\delta = 24.7$ ppm). The typical ^{1}H NMR signal of ethyl methacrylate (δ, ppm: 6.05, 1H, br; 5.3, 1H, br; 4.25, 2H, q; 1.80,

2H, br, 1.25, 3H, t) was observed as well as the signal of acetone.

RESULTS

General Remarks

Scheme 1 shows the reactions taking place during decomposition of alkoxyamine Y-R in different conditions. When alkoxyamine Y-R is heated in solution, it can either (i) decompose with formation of alkyl R• and nitroxyl Y• radical pair in the solvent cage, or (ii) form alkene R(-H) and hydroxylamine Y-H by ionic mechanism—intramolecular proton transfer IPT. Alkyl/nitroxyl radical pair can recombine with reformation of parent alkoxyamine, undergo H-transfer reaction with formation of diethylphosphite and hydroxylamine Y-H (k_{gem}), or escape from the solvent cage producing radicals in the bulk. It should be mentioned that in-cage H-transfer and intramolecular reaction cannot be distinguished in our experiment. When radicals escape from the solvent cage, in the absence of scavenger/reductant the radicals R• and Y• can recombine (iii) or undergo H-transfer reaction by radical mechanism (iv). Furthermore, two alkyl radicals can recombine or disproportionate (v).

If no H-transfer (ii) or (iv) occurs for a particular alkoxyamine, then the Persistent Radical Effect (PRE)[24] takes place. In this case, the kinetics of alkoxyamine decomposition is described by eq 1:

$$[RY]_{(t)} = [RY]_{(t=0)} - [RY]_{(t=0)}{}^{2/3} \cdot \left(\frac{3k_d^2 \cdot 2k_t}{k_c^2}\right)^{1/3} \cdot t^{1/3} \quad (1)$$

If the H-transfer reaction is present [either due to the intramolecular or radical mechanism, reactions (ii) and (iv)], the quantitative formation of hydroxylamine/amine and alkene R(-H) as final reaction products is observed. The particular mechanism can be determined by the thermolysis of alkoxyamine in the presence of scavenger. The addition of scavenger PhSH suppresses reactions (iii)–(v), whereas reactions of nitroxyl and alkyl radicals with thiophenol (vi) and (vii) lead to the formation of alkane RH and hydroxylamine Y-H or amine, respectively.[34,37] If the presence of PhSH has no effect on reaction (ii),[38] the existence of alkene R(-H) in the reaction medium during thermolysis indicates intramolecular/in-cage H-transfer reaction.

Mechanism and Kinetics of Decomposition Of Alkoxyamines 1–4 in the Presence of Scavenger: the Absence of IPT

The decomposition of 20 mM of alkoxyamines **1, 2,** and **4** has been carried out in the presence of scavenger, and the quantitative formation of alkane RH has been observed by ^{1}H NMR [Fig. 2(a,b) and Table 1, entries 1–3]. Furthermore, a loss of 40 mM of PhSH has been found as expected for the scavenging of alkyl radical and the reduction of nitroxide. The formation of the nitroxide as an intermediate during the thermolysis of SG1-based alkoxyamines has been evidenced using EPR previously. This highlights that the C—ON bond homolysis is the only process occurring during decomposition of the alkoxyamines [Scheme 1, reaction (i)]. At the same time, the amount of hydroxylamine/amine[41] formed was much lower than expected ($\sim$ 13–16 mM). This fact is easily understood, since, according to literature, nitroxide or subsequent hydroxylamine Y-H (formed after reduction of SG1 in the presence of H-donor) are unstable at elevated temperatures.[42,43] To verify this, we investigated the decomposition products of SG1 in the absence/presence of H-donor under our experimental conditions. The decomposition half-time of 0.1 mM of SG1 in benzene at 75 °C was equal to 123 h (monitored using EPR). As under our experimental conditions, the stability of SG1 is sufficient not to alter the alkoxyamine decomposition, the products of SG1 decomposition have not been investigated.

Assuming that the conversion of SG1 into Y-H at room temperature in the presence of PhSH is complete, the formation of diethylphosphite at $T = 75$°C is quantitative with the rate constant of Y-H decomposition equal to 0.03 s^{-1} (Supporting Information Fig. 1). Thus, in most cases (see below), the presence of diethylphosphite is a signature of the Y-H being an unstable intermediate. Taking into account the release of diethylphosphite due to Y-H decomposition, the amount of diethylphosphite (6–4 mM, entries 1–3 in Table 1) affords a correct mass balance in phosphorus compounds.

The kinetics of alkoxyamine decay in the presence of scavenger is monoexponential (Supporting Information Fig. 2). As no R(-H) has been detected and 100% of alkane RH formed, we conclude that no reaction competes with C—ON bound homolysis. The exponential fit of experimental kinetics provides the values of k_d for three alkoxyamines (Table 2 and Supporting Information Fig. 2).

Mechanism and Kinetics of Alkoxyamines Decomposition in the Absence of Scavenger: Evidence of the Intermolecular H-Atom Transfer Reaction

Decomposition of Alkoxyamines 1, 2

The decomposition of **1** in solution degassed under high vacuum [$P = 10^{-5}$ mbar, entry 7, Table 1, Fig. 2(a,c,d)] yields 18 mM of alkene and 17 mM of diethylphosphite. This observation is in good agreement with almost quantitative intermolecular H-transfer reaction [reaction (iv) in Scheme 1] yielding alkene R(-H) and Y-H, which afterward decomposes into diethylphosphite (see above) due to a long duration of experiment. The presence of SG1 (2 mM) is likely due to a disproportionation of Y-H leading to nitroxide, water, and amine (Supporting Information Scheme 2).[44] The latter compound is unstable at this temperature and is expected to decompose into imine and diethylphosphite (retrophosphorylation reaction[8]). That is why no Y-H and phosphorylated amine have been detected.

The decomposition kinetics of alkoxyamines **1** and **2** (48 h, 75 °C) in the absence of scavenger in poorly degassed solutions ($P = 10^{-3}$ mbar) and after freeze-pump-thaw degassing have been measured. They are monoexponential (Fig. 3) and have much slower rate constants (two orders of magnitude) compared with those obtained in the presence of PhSH (Table 2). Independent of the experimental conditions, the

TABLE 1 Reaction Products of Alkoxyamines 1–4 Decomposition in Different Conditions

		Before Thermolysis					After Thermolysis								
Entries	Alkoxyamine	[Alkox], mM	[PhSH], mM	P^a, mbar	[TFA], mM	[Nitroxide], mM	[Alkox], mM	[PhSH], mM	[Alkane], mM	[Alkene], mM	[Hydroxylamine]+ [amine], mM	[Nitroxide], mM	[Diethylphosphite], mM	[1a or 2a or 4a], mM	[Other Unidentified ^{31}P-Containing Products], mM
1	**1**	20	240	10^{-3}	0	0	0[c]	200	19	0	13.5	0[b]	6	0[c]	0[c]
2	**2**	20	165	10^{-3}	0	0	0[c]	125	19	0	13	0[b]	6	0[c]	0[c]
3	**4**	20	140	10^{-3}	0	0	0[c]	105[d]	19	0	16	0[b]	4	0[c]	0[c]
4	**1**	20	0	10^{-3}	0	0	0[c]	–[e]	0[c]	5	0[e]	2	3	14	0[c]
5	**2**	20	0	10^{-3}	0	0	3	–[e]	0[c]	3	0[c]	2	4	9	2[f]
6	**4**	20	0	10^{-3}	0	0	1	–[e]	0[c]	Traces	0[c]	4	8	0[c]	6[g]
7	**1**	20	0	10^{-5}	0	0	0[c]	–[e]	0[c]	18	0[c]	2	17	Traces	0[c]
8	**4**	20	0	10^{-5}	0	0	7	–[e]	0[c]	Traces	0[c]	0[b]	7	Traces	5[f]
9	**1**	20	0	10^{-3}	22	0	0[c]	–[e]	0[c]	2	0[c]	0[b]	8	12	0[c]
10	**4**	20	0	10^{-3}	22	0	0[c]	–[e]	0[c]	Traces	0[c]	0[b]	5	0[c]	14[h]
11	**1**	20	0	10^{-3}	0	40	1	–[e]	0[c]	9	0[c]	–[i]	8	10	0[c]
12	**4**	20	0	10^{-3}	0	40	4	–[e]	0[c]	1	0[c]	–[i]	4	Traces	12[h]

Accuracy of 0.5 mM for concentrations.
[a] *P*, residual pressure in the sample after degassing.
[b] Not detected by EPR (threshold for the detection is 10^{-5} M).
[c] Not detected (threshold of 1 mM).
[d] Very broad line of the PhS-*H* signal increased the error on the estimate of concentration.
[e] Absent as starting materials.
[f] Several phosphorous-containing compounds with ^{31}P chemical shift $\delta = -10$ to 5 ppm.
[g] One compound with ^{31}P chemical shift $\delta = -0.03$ ppm.
[h] Several phosphorous-containing compounds with ^{31}P chemical shift $\delta = -10$ to 30 ppm.
[i] Not estimated.

TABLE 2 Kinetic Parameters of Decomposition of Alkoxyamines 1–2, 4 Under Various Conditions at $T = 75$ °C

	Decomposition in the Presence of Scavenger,[a] $k_d \times 10^3$ (s^{-1}) (E_a, kJ mol^{-1})[b]	Decomposition in the Presence of Scavenger and TFA (1.1 equiv), $k_d' \times 10^3$ (s^{-1}) (E_a, kJ mol^{-1})[b]	Decomposition in the Absence of Scavenger ($P = 10^{-3}$ mbar), $k_{obs} \times 10^5$ (s^{-1})	Decomposition in the Absence of Scavenger ($P = 10^{-5}$ mbar), $k_{obs}' \times 10^5$ (s^{-1})
1	15 ± 1 (108.0)	10 ± 1 (109.1)	12 ± 1	3.7 ± 1
2	3.5 ± 0.5 (112.2)	2.0 ± 0.5 (113.8)	1.8 ± 0.5	–
4	5.5 ± 0.5 (110.9)	6.0 ± 0.5 (110.6)	2.2 ± 0.3	0.6 ± 0.05

[a] PhSH as scavenger (7–12 equiv.).

[b] Error commonly accepted is 1–2 kJ mol^{-1}.

analysis of ^{1}H NMR revealed the formation of alkenes R(-H) [Fig. 1(c,d)] that cannot be ascribed to the disproportionation [reaction (v), Scheme 1], because no formation of alkane RH has been observed. Thus, it can be concluded that R(-H) is formed during H-atom transfer reaction (reaction (ii) in Scheme 1).

Note, that in poorly degassed solution, (entries 4 and 5, Table 1) the amounts of alkene were much lower (<5 mM) than those in solution degassed under high vacuum (entries 7), whereas the amounts of decomposed alkoxyamines were found larger. On the other hand, a new phosphorus-containing compound was formed ($\delta = 24.7$ ppm in ^{31}P NMR spectrum). To identify the structure of new product, a quantitative decomposition of alkoxyamine **3** with subsequent product analysis using mass spectrometry has been performed. The obtained results indicate the loss of C_3H_6 fragment by the molecule **3**, whereas the ^{31}P NMR is typical for alkoxyamine. The results obtained using ^{1}H, ^{31}P NMR, and mass analyses confirm the assignment of this product to the molecule **3a**. The formation of products having similar structure (i.e., alkoxyamines with the carboxylic group directly bound to the nitroxyl moiety) **1a** and **2a** (Scheme 1) has been expected during decomposition of alkoxyamines **1** and **2**.

The account of phosphorus compounds [alkoxyamines **1a** and **2a,** alkene R(-H)] afforded a good mass balance. For **1**, the sum of nitroxide and diethylphosphite concentrations corresponds to the concentration of generated diethylphosphite (entry 4, Table 1) implying that the SG1 is observed due to the reoxidation of Y-H by residual oxygen. For **2**, the same sum is larger, meaning that the other processes are involved during the decomposition of this alkoxyamine. We suppose that this difference is determined by roughly 10 times longer decomposition time of alkoxyamine **2** compared with that of **1** (Table 2). Because of the longer time of decomposition the *tert*-butoxy group of **2a** can be hydrolyzed[45] and afford **4a,** which then decomposes into diethylphosphite (as proposed in Supporting Information Scheme 2). Thus, a part of Y-H is reoxidized into SG1, and another part is decomposed into diethylphosphite or some other side-products (entry 5, Table 1).

Different behaviors depending on the experimental conditions lead to the differences in kinetics exemplified for **1** in Figure 3. This indicates the high impact of oxygen on the decomposition mechanism of SG1-based alkoxyamines.

Decomposition of Alkoxyamine 4

The decomposition of **4** (entry 8, Table 1) in solution degassed under high vacuum leads to dramatically different results in comparison with decomposition of **1**, **2**, **3**. Decomposition of 13 mM of alkoxyamine yields 7 mM of diethylphosphite and only traces of alkene. These results mean that the presence of carboxylic function in alkoxyamine involves different pathway of decomposition due to intramolecular H-bonding[46,47] as tentatively is displayed in Supporting Information Scheme 3. In addition, degradation of SG1 can be induced by the acid leading to various side-products. These degradation routes are faster than the intermolecular H-transfer reaction, leading to diethylphosphite, and some other phosphorus compounds formed in the process different to those mentioned above. The amount of detected phosphorus compounds afforded a good mass balance (12 mM).

In poorly degassed solution, the decomposition products of alkoxyamine **4** show only traces of alkene. Contrary to decomposition of alkoxyamines **1**, **2**, **3** the signals of **4a** are absent in NMR spectra [entry 6, Table 1, Fig. 2(c,d)], whereas a signal around 0 ppm is observed by ^{31}P NMR. Note that carbonic acid derivative **4a** is not expected to be stable at 75 °C and should decompose into CO_2 and Y-H (Supporting Information Scheme 4). The latter should be reoxidized into SG1 by the residual oxygen (entry 6, Table 1). The sum of phosphorus compounds affords a good mass balance.

Influence of Acid and Additional Nitroxide on the Decomposition

To confirm the occurrence of IHAT, the decomposition of **1** and **4** has been studied in the presence of additional nitroxide SG1 (entries 11 and 12, Table 1). As the addition of SG1 increases the probability of alkyl radical decay via reaction (iv) Scheme 1, it was expected that the H-atom transfer in these reactions leads to the formation of larger amount of alkene during the decomposition. Indeed, this trend has been observed in the experiment: when alkoxyamines **1** and **4** decomposed in the presence of 40 mM of SG1 in poorly degassed solution, the formation of 9 and 1 mM of alkene was observed, respectively (entries 11 and 12 in Table 1). This confirms that intermolecular H-transfer reaction occurs both for ester and carboxylic fragments, and that reaction is very slow and cannot compete with other decomposition pathways for the carboxylic fragment.

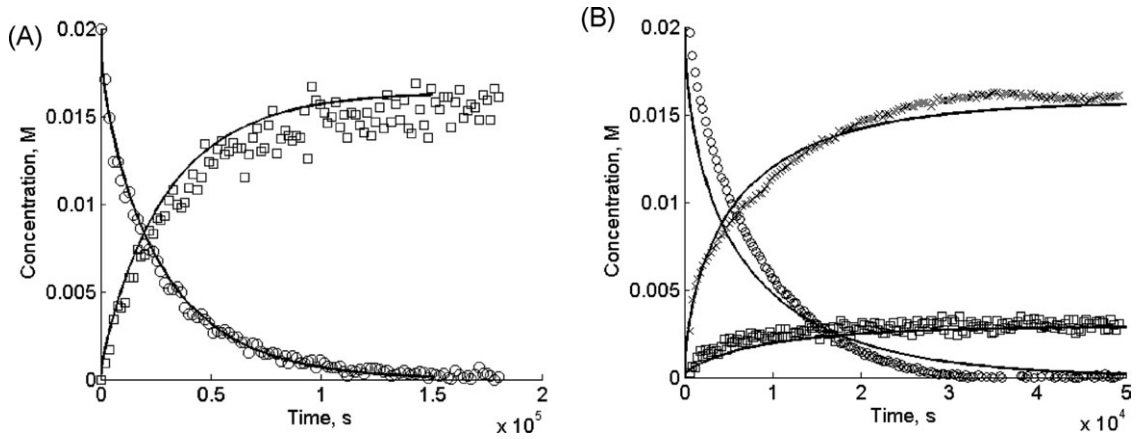


FIGURE 3 Experimental (symbols) and calculated (full line) kinetics for decomposition of alkoxyamine**1** in the absence of scavenger for solution degassed under high vacuum (a) and for poorly degassed solution (b): (○) alkoxyamine, (□) alkene, (+) oxygen product, solid line, calculated kinetics; see text and Supporting Information Table 1 for details.

The difference in thermolysis of alkoxyamines **1**, **2**, **3**, and **4** could be caused by the influence of carboxylic function in **4** on the rate of alkoxyamine homolysis. Recently, Mazarin et al.[48] have shown that the protonation of the nitroxide fragment should slow down the homolysis and, hence, favor side reactions such as the C—P bond cleavage.[49] Edeleva et al. reported that the protonation of designed nitroxide fragments significantly decreases the C—ON homolysis rate constant.[50] To test the influence of carboxylic function in **4** on the rate of alkoxyamines homolysis, decomposition of **1** in the presence of PhSH has been investigated in the presence of 1.1 equiv. of trifluoroacetic acid (TFA, entry 9, Table 1). It has been found that the addition of 1.1 equiv. of TFA does not decrease k_d values for **1**, **2**, and **4** significantly, which should take place if some new processes occur.[51–53] This fact is in a good agreement with results obtained by Marque et al.,[53] that is, that E_a values obtained in the presence of TFA are not larger than 1.6 kJ mol^{-1} in comparison with the normal ones.[54]

In the absence of scavenger in acidic medium, the decomposition of alkoxyamine **1** proceeds slower compared with the nonacidic media, which evidently is due to the retardation of homolysis. The amount of alkene formed in the presence of acid is smaller compared with nonacidic conditions, showing nearly twofold decrease for alkoxyamine **1** (Supporting Information Fig. 4, entries 1 and 9 in Table 1). Thus, the presence of acid decreases the impact of H-transfer reaction in the decomposition of alkoxyamines **1**, **2**, **3**. On the other hand, the presence of acid shows nearly no effect on the kinetics of the decomposition of **4** (entries 4 and 10, Table 1): as **4** carries already a carboxylic group, the addition of extra acid has a small effect.

It is well known that nitroxides are unstable under acidic condition.[53,55] Consequently, the decrease of nitroxide concentration will decrease the contribution of the reverse reaction, and hence of the side reactions. Furthermore, the decomposition of nitroxide leads to several by-products (not identified here) which can scavenge alkyl radicals in another way by suppressing the formation of alkene. Consequently, the results observed under acidic conditions for **4** are likely due to a kinetic effect and processes involving degradation products. The occurrence of kinetic effect is supported by the recent results reported by Ansong et al.[56,57] who have shown that the NMP of MMA is possible using TEMPO under harsh acidic conditions. As alkoxyamine **4** carries a carboxylic function on the alkyl fragment, it plays the role of extra acid for **1**, implying the absence of alkene.

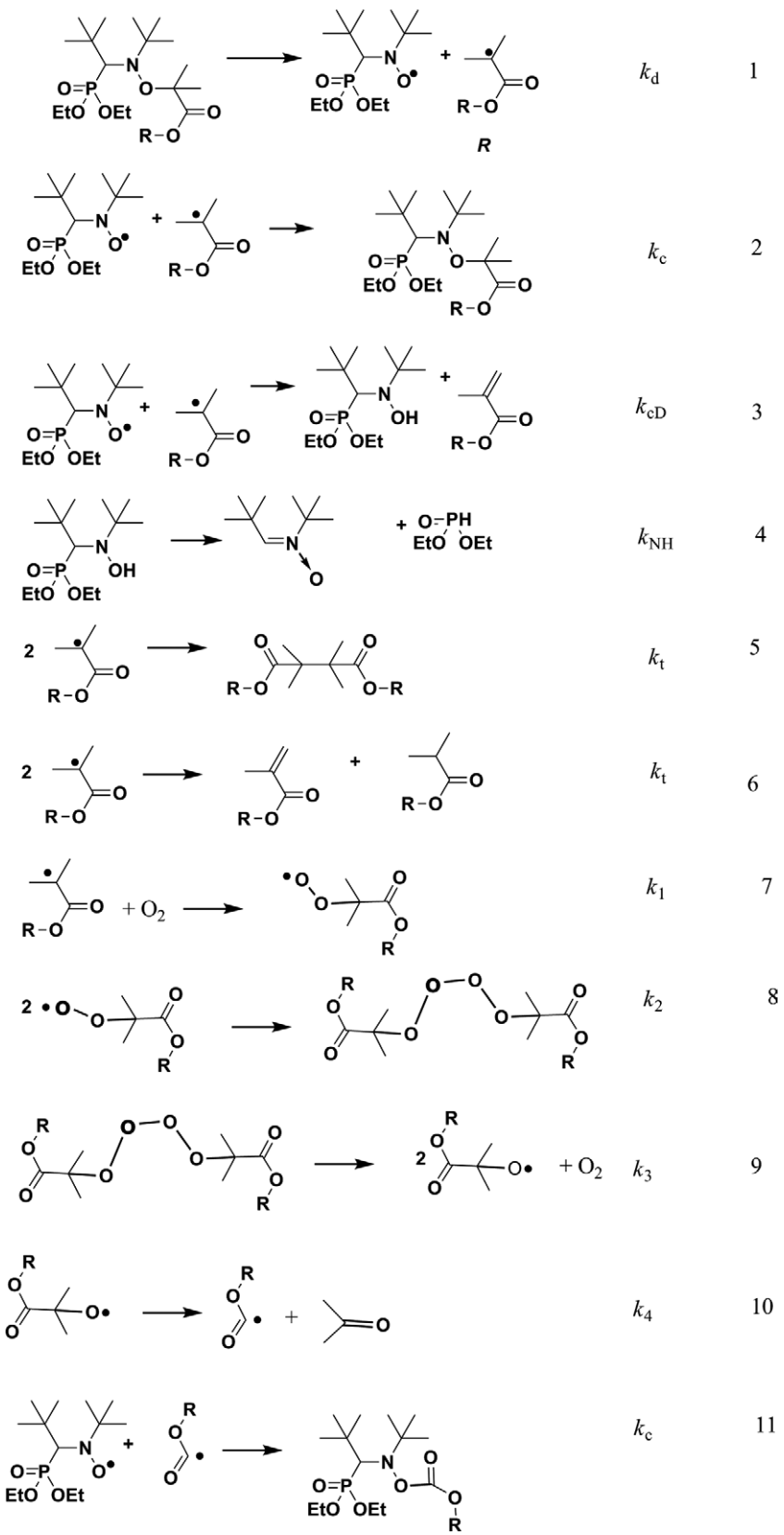
Modeling the Mechanism of Decomposition of SG1-Based alkoxyamines

To confirm the proposed mechanism for SG1-based alkoxyamines, we performed simulations of experimental results for alkoxyamine **1**. The following reactions have been taken into account for modeling the products ratios and kinetics of alkoxyamine decomposition in highly degassed solution: the homolysis of alkoxyamine (reaction 1 in Scheme 2), the reformation of the alkoxyamine (reaction 2 in Scheme 2), the side reaction of intermolecular H-atom transfer (IHAT, reaction 3), the decomposition of hydroxylamine Y-H (reaction 4 in Scheme 2) and the self-termination reactions (reactions 5 and 6 in Scheme 2). In our simulations, we used the values of k_d measured in this article and those listed in Table 2. These values are in good agreement with those already reported in the literature.[31,58,59] The values of $k_c = 1.5 \times 10^6$ M^{-1} s^{-1} were assumed to be independent of the alkyl fragment of the ester function (Supporting Information Table 1).[60] The k_{NH} measured in this paper is equal to 0.03 s^{-1}, and the rate constant for the conventional self-termination reactions $k_t = 2 \times 10^7$ M^{-1}s^{-1} is found in the literature.[61] The value of k_{cD} has been estimated using eqs 2 and 3:[23]

$$f_D = \frac{k_{cD}}{k_c + k_{cD}} \quad (2)$$

$$\left[R^1R^2NOR\right]_t = \left[R^1R^2NOR\right] \cdot \exp(-f_D \cdot k_d \cdot t) \quad (3)$$

where f_D is the H-transfer factor. This factor determines the regime of NMP (controlled character and liveliness). For f_D larger than 3% NMP experiment fails, whereas for f_D smaller



SCHEME 2 Reactions involved into the decomposition mechanism of SG1-based alkoxyamines in the absence of scavenger and in nonacidic conditions.

than 0.5%, there should be no significant effect of reaction 3 (Scheme 2) on NMP.

The reactions involving oxygen and alkyl radicals were described by reactions 7–11 (Scheme 2).[62,63] In particular, alkyl radical is scavenged by oxygen with the formation of alkyperoxyl radical (reaction 7). The latter self-terminates yielding dialkyltetraoxide (reaction 8). The dialkyltetraoxide collapses spontaneously into alkoxyl radicals and oxygen (reaction 9). As there is no possibility of H-abstraction by alkoxyl radicals, the β-fragmentation (reaction 10) could be the main process leading to formation of acetone and alkoxycarbonyl radical. The latter reacts very fast by coupling with the nitroxide (reaction 11). For the sake of simplicity, the rate constant of reaction 11 was assumed to be similar to k_c.

Reaction of oxygen with alkyl radicals is almost self-diffusion controlled (10^9–10^7 $M^{-1}s^{-1}$)[61] and has been assumed to occur with the rate constant $k_1 = 10^7 \times M^{-1}s^{-1}$. The impact of this reaction depends on the amount of oxygen and is therefore given by k_1^* in eq 4:

$$k_1^* = k_1 \cdot [O_2] \quad (4)$$

Oxygen concentration in air-saturated benzene solution is 2.0 mM.[65,66] Using EPR oxymetry (see Supporting Information for experimental details) we estimated oxygen concentration under our experimental conditions to be 10^{-4} M, which disagrees with an important impact of oxygen on the reactivity observed. However, taking into account the gas-solution equilibrium due to the presence of atmospheric gas above the liquid sample, we assumed constant oxygen concentration during the decomposition experiment. Therefore, the reaction of alkyl radicals with oxygen was considered as monomolecular in calculations (eq 4) with the rate constant $k_1^* = 1.5 \times 10^3$ s^{-1}.The literature rate constant for the self-termination of alkyl peroxyl is about 10^4 $M^{-1}s^{-1}$ and does not depend on the alkyl fragment.[63] The collapsing reaction of the subsequent dialkyltetraoxide was assumed to occur instantaneously. The values of k_3 were estimated from the activation energy (E_a = 10–15 kJ mol^{-1}) and the activation factor $A_0 = 10^{13}$ s^{-1} for the β-fragmentation of *tert*-butoxyl radical.[67] The parameters providing for the best fit of the experimental data (listed in Supporting Information Table 1) are close to the values reported in the literature. The results of the calculations are shown in Figure 3.

DISCUSSION

Intermolecular H-Atom Transfer

The decomposition of SG1-based alkoxyamines in the presence of scavenger proceeds via formation of nitroxide and alkyl radical and their subsequent reaction with PhSH. The hydroxylamine/amine YH formed in the latter reaction undergoes decomposition with formation of diethylphosphite. It should be emphasized that no intramolecular/in-cage H-transfer has been detected during the decomposition.

In the absence of scavenger and in "highly degassed solution" (10^{-5}–10^{-6} mbar), decomposition of SG1-based alkoxyamines **1** proceeds with IHAT. The analysis of our experimental results allows us to obtain the value of k_{cD} equal to 1.7×10^3 $M^{-1}s^{-1}$ at 75 °C, which is in good agreement with that reported by Dire et al. ($k_{cD} = 1.69 \times 10^3$ $M^{-1}s^{-1}$ at 70 °C) for the IHAT process occurring with poly(methyl methacrylate) radical. For alkoxyamine **1**, which is a basic model for polymeric alkoxyamine, f_D of about 0.1% has been estimated. Thus, for alkoxyamine **1** NMP of MMA should not be spoiled by the IHAT process. On the other hand, a very different behavior has been observed for alkoxyamine **4**, that is, only traces of alkene have been detected, which means negligible contribution of IHAT process. This fact reveals the strong impact of a carboxylic function on the side reactions in alkoxyamine decomposition. In particular, the role of IHAT process decreases due to appearance of different pathway of decomposition for alkoxyamine **4**.

Role of Oxygen

In most polymerization experiments, degassing is usually performed by conventional oil pump (10^{-3} mbar), and often only bubbling by gases such as nitrogen or argon is used. Therefore, to investigate the role of the residual oxygen, we also performed the homolysis of alkoxyamine **1** and **2** in solution degassed under low vacuum (10^{-3} mbar). It has been found that degassing strongly affects the amount of alkene concentration in reaction products, in particular only a very small amount of alkene has been detected under low vacuum (25%) instead of 90% at high vacuum. At the same time, the starting materials completely decomposed and the formation of new phosphorus species identified as an ester of hydroxylamine (**1a** and **2a**) has been observed. We suppose that the hydroxylamines **1a** and **2a** are formed due to scavenging of alkyl radicals by oxygen yielding alkylperoxyl radicals, which dimerize into tetraoxide. The latter collapse instantaneously to yield alkoxyl radicals, which undergo β-fragmentation and afford acyl radical scavenged by the nitroxide. Such types of reactions of oxidation are well documented.[62,63] Thus, according to the literature and our results, Scheme 2 has been proposed to describe the effect of oxygen on the decomposition of alkoxyamines. Good simulations were obtained for the kinetics of alkoxyamine **1**, alkene and **1a** by small adjustment of the rate constants. Noteworthy, the new alkoxyamines exhibit very close ^{31}P NMR shifts to those of starting materials, and this might lead to misinterpretation of results.

The expected influence of oxygen concentration on decomposition kinetics is shown in Figure 4(a). In agreement with experimental results, calculated kinetics depends on the amount of residual oxygen. It varies from fast decay ($[O_2]$ = 10 mM, saturated solution), that is, complete scavenging, to no effect ($[O_2]$ = 0.01 mM) [Fig. 4(a)]. However, as the amount of oxygen cannot be rigorously controlled, the effect of alkoxyamine concentration at constant oxygen concentration has also been investigated [Fig. 5(b)]. As expected, the experimental decay of alkoxyamine accelerates as the concentration decreases. In experiments performed with concentrations of 20 and 5 mM of **1**, a twofold decrease of k_{obs}

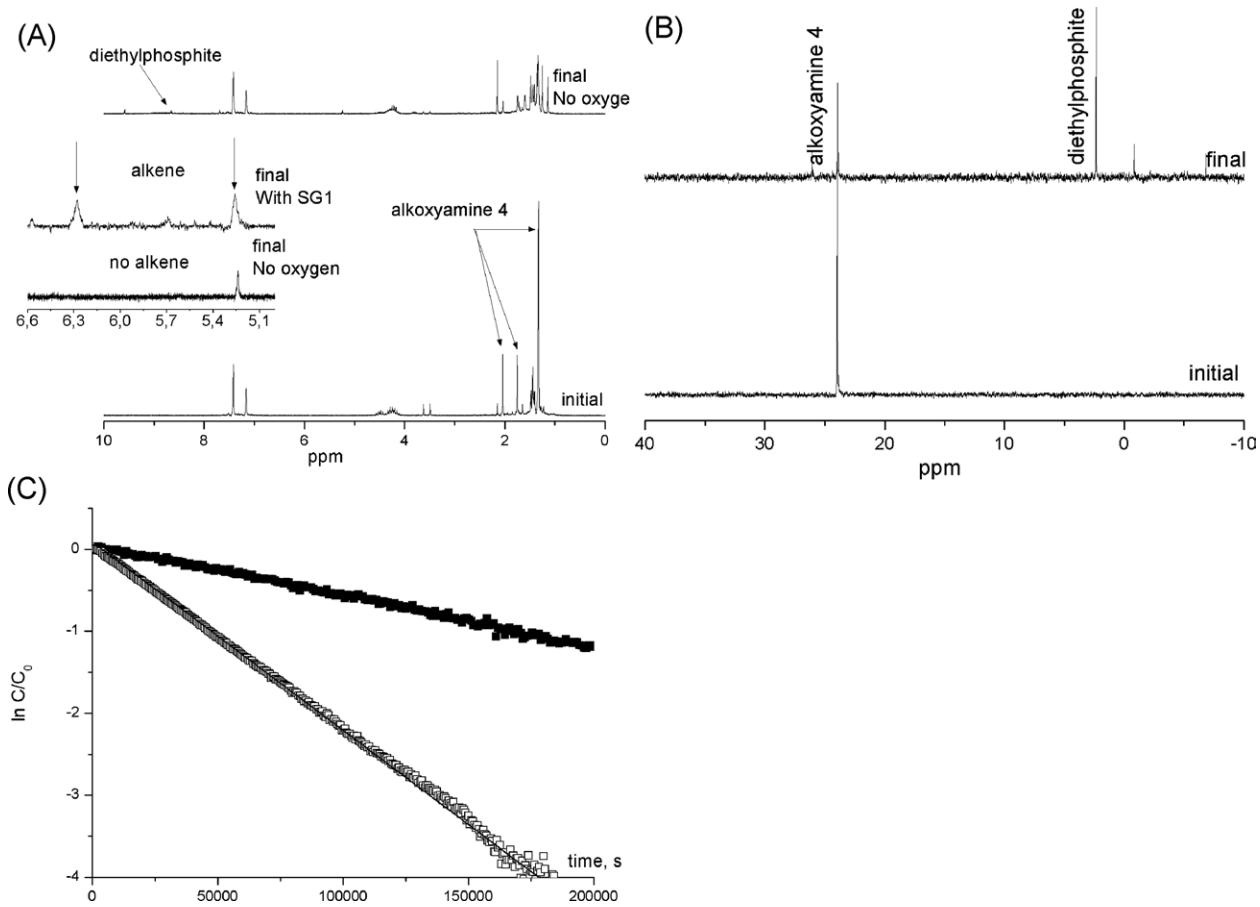


FIGURE 4 (a) ^{1}H NMR and inset: ^{1}H NMR spectra after decomposition of alkoxyamine **4** in the absence of oxygen and in the presence of 2 eq. of SG1. Arrows indicate the position of alkene signals (5.2, 6.3 ppm).[68] (b) ^{31}P NMR detected before (bottom) and after (top) decomposition of alkoxyamine **4** (0.02 M solution in benzene, d_6) in the absence of scavenger; $T = 75$ °C. (c) Decomposition kinetics of alkoxyamine in the absence of scavenger at 10^{-3} mbar (□) and 10^{-6} mbar (■) of residual pressure, line shows linear fit of the experimental data points.

has been observed as expected, which supports the robustness and the validity of Scheme 2.

The Reasons for Uncontrolled Polymerization of MMA in the Presence of SG1 Nitroxide

As has been found above, the k_{cD} for SG1-based alkoxyamine **1** has been estimated as 1.7×10^3 $M^{-1}s^{-1}$ implying f_D values around 0.1%, clearly below the threshold of any impact on NMP.[2,6,24] However, as was already mentioned above, NMP of MMA in the presence of SG1 nitroxide is unsuccessful.[25] In fact, $k_{c,ds}$ for poly(methyl methacrylate) radical recombination with SG1 has been reported as 2.0×10^4 $M^{-1}s^{-1}$ leading to $f_D = 10\%$ for the polymeric species and spoiling the NMP experiment as observed.[28] These results highlight the importance of an accurate and reliable estimate of both k_c and $k_{c,ds}$ values to predict NMP.

"Hence, what are the real reasons for the unsuccessful controlled NMP of MMA using SG1?" In fact, few years ago, using the Fischer's diagram approaches, we showed that k_d and k_c values of the corresponding macromolecular alkoxyamine are not suitable for NMP when the effect of the penultimate unit is accounted for.[25] Besides the fact that both high homolysis rate constant and low reformation rate constant of alkoxyamine favor strongly the self-termination reactions of macroalkyl radicals, which would lower the quality of NMP, they favor also the occurrence of the IHAT side reaction, dramatically spoiling any chance to perform successful homopolymerization of MMA by NMP.

"The next question is why the NMP of MMA using SG1 becomes successful if a few percents of styrene (S) are added?" A few years ago, it was shown that three dyads MMA-MMA-SG1, S-MMA-SG1, and MMA-S-SG1 are involved in NMP process, and the success of NMP is ensured by the dormant species MMA-S-SG1. The structure reactivity relationships developed by the authors of this paper[68] afforded the k_d values of 0.01 s^{-1}, 0.003 s^{-1}, and 2.2 10^{-4} s^{-1}, and the k_c values as 2×10^4 $M^{-1}{\cdot}s^{-1}$,[69] 10^5 $M^{-1}{\cdot}s^{-1}$,[70] and 6×10^4 $M^{-1}{\cdot}s^{-1}$ [71] for MMA-MMA-SG1, S-MMA-SG1, and MMA-S-SG1, respectively. Consequently, the relationship $k_{d,MMA\text{-}S\text{-}SG1} < k_{d,MMA\text{-}MMA\text{-}SG1}$, $k_{c,S\text{-}MMA\text{-}SG1} > k_{c,MMA\text{-}MMA\text{-}SG1}$ $f_{D,S\text{-}MMA\text{-}SG1} = 2\% < f_{D,MMA\text{-}MMA\text{-}SG1} = 10\%$, $k_{c,MMA\text{-}S\text{-}SG1} > k_{c,MMA\text{-}MMA\text{-}SG1}$, and $f_{D,MMA\text{-}S\text{-}SG1} <<< f_{D,MMA\text{-}MMA\text{-}SG1}$ [72] predicts that the IHAT

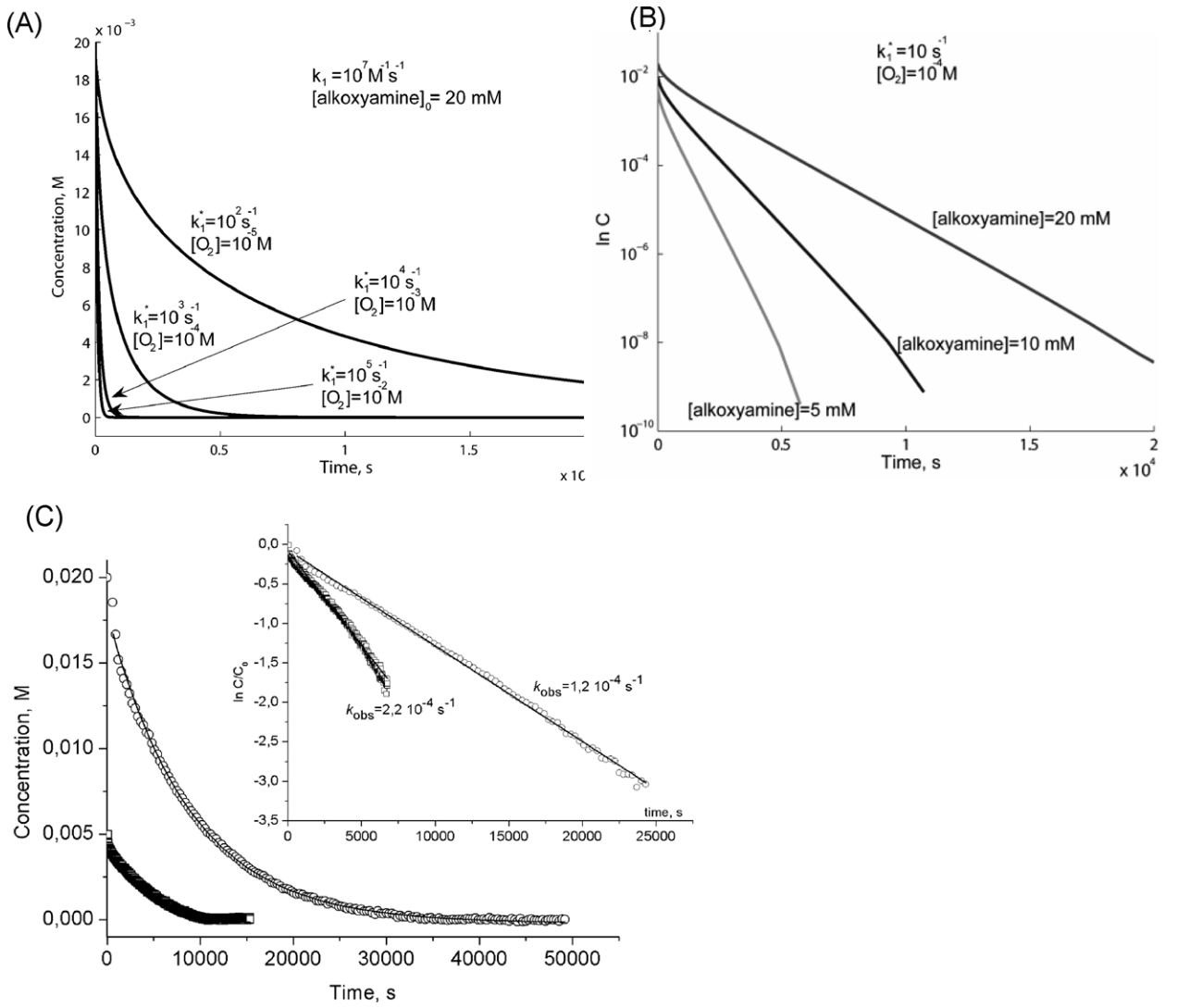


FIGURE 5 Calculated kinetics of alkoxyamine **1**: (a) at 0.02 M initial concentration in the presence of different oxygen concentrations; (b) at initial oxygen concentration 0.1 mM and different alkoxyamine concentrations. The calculations were performed according to eqs 1, 2, and 5–7 (Scheme 2). Rate constants are listed in Supporting Information Table 1. The values of k_1 and k_1^*, oxygen and alkoxyamine concentrations are given in the figures. (c) Experimental kinetics of decomposition of alkoxyamine **1** in the absence of scavenger at 5 mM (□) and at 20 mM (○) solution in the presence of 0.1 mM of oxygen (for solution degassed under 10^{-3} mbar and as given by EPR oxymetry measurement, see Supporting Information) and subsequent exponential fit. The observed decomposition rate constants are given in the figure.

process due to the MMA moiety is dramatically lowered and has almost no effect on the fate of the NMP experiment (livingness larger than 75%). Furthermore, these results show that IHAT process does not depend on the effect of the penultimate unit and on the chain length of the polymeric radical. Consequently, calculations using simple models could provide insights to the requirements for the IHAT facilitating and, hence, to the design of the most suitable alkoxyamine for a successful NMP of MMA.

CONCLUSIONS

In this contribution, we have studied the decomposition mechanism and kinetics of SG1 and isobutyl alkyl fragments-based alkoxyamines at different conditions. The possible side reactions that alter NMP have been evaluated. Analysis of reaction products of decomposition in the presence of alkyl radicals scavenger or nitroxide reducing agent has shown that these alkoxyamines undergo primary NO—C bond homolysis, that is, no IPT occurs. When the decomposition of **1** is performed in nonscavenging conditions (and in solution degassed under high vacuum), IHAT process is observed, despite it is often claimed to be a negligible process. The k_{cD} value has been estimated as 1.7×10^3 $M^{-1}s^{-1}$.

On the other hand, the decomposition of SG1-based alkoxyamines performed in poorly degassed solution in nonscavenging conditions reveals high impact of oxygen on decomposition mechanism. Indeed, nearly quantitative formation of

oxidation product has been observed. Such degassing procedure is currently applied both to investigate kinetics and to perform polymerization experiments, and, consequently, may cause a misleading discussion of the results. Furthermore, the NMR shift of these new compounds is very close to those of starting materials that may also be misleading. However, such oxidation events are expected to occur only when IPT or IHAT processes are low or in the absence of efficient scavenger (as alkene in polymerization experiments).

We have observed that the presence of acid (extra addition or carboxylic function on alkyl or nitroxide fragments) affords also unexpected results, for example, a striking decrease of generated alkene. This observation has been ascribed to a kinetic effect likely due to the instability of nitroxide in the presence of acid. This effect has already been applied by Ansong[56,57] to reduce dramatically the IHAT process with TEMPO and to perform partly successful NMP of MMA under harsh acidic conditions.

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39 ^{1}H NMR chemical shifts (δ, 200 MHz, C_6D_6): 1–1.07 s 9H, 1.10, 1.24 t 6H, 1.37 s 9H, 1.73, 1.77 s 6H, 3.40 s 3H, 3.94, 4.53 br 4H, alkane −1.02 d 6H, 2.33 septpl 1H, 3.33 s 3H, alkene −1.80 br 3H, 5.17, 6.08 br 1H, diethylphosphite −0.93, 1.05 d of tr 6H, 3.75, 3.94 br 4H, 8.29, 9.17 s 1H. ^{31}P NMR chemical shifts: −22.5 ppm, diethylphosphite −3.02 ppm, SG 1-H −27.0 ppm.

40 ^{1}H chemical shifts (δ, 200 MHz, $C_6D_4Cl_2$):1–1.30 s 9H, 1.47 s 9H, 1.91 s 6H 3.47, 3.60 s 1H, 3.87 s 3H, alkene −6.08, 5.18 br 1H, 1.86 br 2H, diethylphosphite −1.39 db tr 6H, 4.21 br 4H, 8.65, 9.58 s 1H, acetone −1,55 ppm (s, 6H). ^{31}P chemical shifts: 1–22.5 ppm, diethylphosphite −3.02 ppm, diethyl 1-(tert-butyl(-methoxycarbonyloxy)amino)-2,2-dimethylpropylphosphonate (oxidation product) −22.0 ppm.

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67 ^{1}H chemical shifts (δ, 200 MHz, $C_6D_4Cl_2$): 4–1.32 s 9H, 1.33 s 9H, 1.44 db of t 6H, 1,.75, 2.04 s 6H, 3.49, 3,62 s 1H, 4.25, 4.47 br 4H, alkene −1.8 br 2H, 5.2 br 0.5H, 6.3 br 0.5H, diethylphosphite −1.39 dbtr 6H, 4.21 br 4H, 8.65, 9.58 s 1H. ^{31}P chemical shifts: 4–23.8 ppm, diethylphosphite −3.02 ppm.

68 Personal communication of the authors. *Chem. Rev.,* in preparation.

69 $\upsilon = 1.96$, $\sigma_I = 0.09$, $\sigma_{RS} = 0.20$. $\upsilon_1 = \upsilon_{t\text{-Bu}} = 1.24$, $\upsilon_2 = \upsilon_{CMe2\text{-}COOMe} = 1.43$, and $\upsilon_3 = \upsilon_{COOMe} = 0.9$. $\sigma_{I,CH2CMe2COOMe} = 0.02$. It was assumed that the penultimate unit had no effect on the radical stabilization.

70 $\upsilon = 1.77$, $\sigma_I = 0.09$, $\sigma_{RS} = 0.20$. $\upsilon_1 = \upsilon_{t\text{-Bu}} = 1.24$, $\upsilon_2 = \upsilon_{CH\text{-}MePh} = 0.99$, and $\upsilon_3 = \upsilon_{COOMe} = 0.9$. $\sigma_{I,CH2CMeHPh} = 0.02$. It was assumed that the penultimate unit had no effect on the radical stabilization.

71 $\upsilon = 1.43$, $\sigma_I = 0.05$, $\sigma_{RS} = 0.34$. $\upsilon_1 = \upsilon_{i\text{-Pr}} = 0.76$, $\upsilon_2 = \upsilon_{CMe2\text{-}COOMe} = 1.43$, and $\upsilon_3 = \upsilon_{Ph} = 0.57$. $\sigma_{I,CH2CMe2COOMe} = 0.02$. It was assumed that the penultimate unit had no effect on the radical stabilization.

72 As the penultimate unit has no effect on the IHAT process (see text), the IHAT process due to the styryl radical is so weak that it cannot be detected.