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Comparative Study on Decomposition Rate Constants for Some Alkoxyamines

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ABSTRACT: The decomposition rate constants k_{dec} as well as the activation rate constants k_{act} of some alkoxyamines were determined and compared with regard to their structures. The results showed that decomposition depends predominantly on steric factors, while both steric and polar factors affect k_{act}. Bulky nitroxides are less susceptible to decomposition probably due to the sterically congested transition state in this reaction. Mechanistically, decomposition was demonstrated to occur bimolecularly. (Namely, the unimolecular pathway is insignificant.) It was also found that alkoxyamines have more chances to undergo decomposition at the deactivation stage than at the activation stage.

Introduction

The recent progress in living radical polymerization (LRP) has opened up novel and facile synthetic routes for providing polymers with well-defined structures.[1] The basic concept of LRP is the alternating activation−deactivation process (Scheme 1a), in which a potentially active (dormant) species P−X is reversibly activated to the reactive radical $P^\bullet$ by thermal, photochemical, and/or chemical stimuli. In the presence of monomer, $P^\bullet$ will undergo propagation until it is deactivated back to P−X. A number of activation−deactivation cycles allow all the chains to have an almost equal opportunity to grow, resulting in the formation of low-polydispersity polymers. Thus, a sufficiently large frequency of activation, i.e., a large activation rate constant k_{act}, is a prerequisite for the system to yield low-polydispersity polymers. The nitroxide-mediated LRP,[2−6] in which X represents nitroxides, is one of the most extensively studied LRPs. In this system, it has been found that k_{act} is strongly affected by the structure of nitroxide both sterically and electronically.[7−9]

Another prerequisite for attaining low polydispersities is to minimize side reactions which permanently deactivate the polymer chains. An important one in the nitroxide system is the decomposition of P−X, in which the nitroxide $X^\bullet$ abstracts the β-H atom of the polymer radical $P^\bullet$, forming a terminally unsaturated polymer $P_{=}$ and a hydroxyamine XH (Scheme 1b).[10−17] As has been reported, the decomposition in an acrylate/DBN system is serious,[18] while that in the corresponding DEPN system is minor,[4,6] which indicates that the structure of nitroxide strongly affects the rate constant of decomposition as well as that of activation, where DBN and DEPN are di-*tert*-butyl nitroxide and *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, respectively (Figure 1). The decomposition also depends on the structure of polymer.[17]

Mechanistically, the β-H abstraction may be assumed to occur in the cage of solvent in both activation and deactivation processes (Scheme 2). Under the condition that the dissociated alkyl radical $P^\bullet$ necessarily reacts with $X^\bullet$, and other reactions such as the termination between $P^\bullet$s are unimportant, we may express the pseudo-first-order decomposition rate constant k_{dec} by[11]

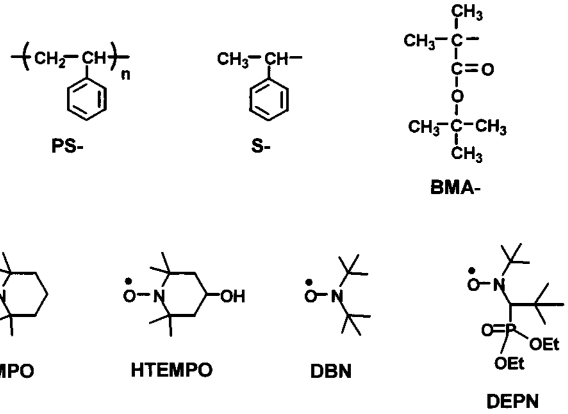

Figure 1. Structures of alkyl groups and nitroxides.

$$k_{dec} = p_{dec}k_{act} \qquad (1)$$

where p_{dec} is the sum of the probabilities of decomposition in the activation and deactivation processes. Thus, a smaller p_{dec} is another important factor for a nitroxide to show high performance. (In these arguments, we rule out the possibility of decomposition being a unimolecular reaction, which will be justified later on.)

The purpose of this work is to determine the p_{dec} of various adducts composed of the alkyl and nitroxyl moieties shown in Figure 1 and make clear the importance of steric and electronic effects on p_{dec}. Fischer et al.[17] have recently studied the decomposition of various alkyl-TEMPO adducts and discussed the effects of alkyl groups on decomposition, where TEMPO is 2,2,6,6-tetramethylpiperidinyl-1-oxy. We in this work will examine the effects of nitroxide groups on decomposition. The results will hopefully be useful for designing effective nitroxides. Another purpose of this work is to rationalize the mechanistic scheme of decomposition shown in Scheme 2. Using the oxygen scavenging technique, we were able to quantitatively discuss the decompositions at the activation and deactivation processes separately.

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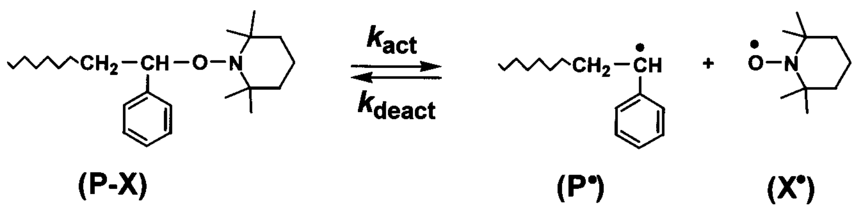
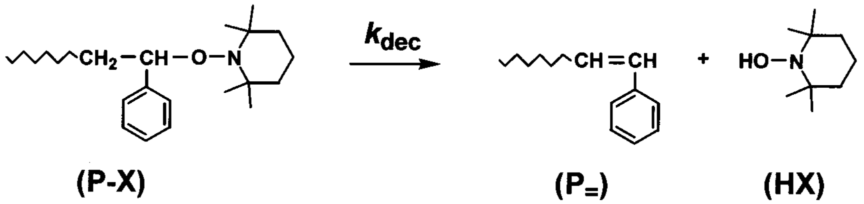
Scheme 1. (a) Reversible Activation and (b) Decomposition

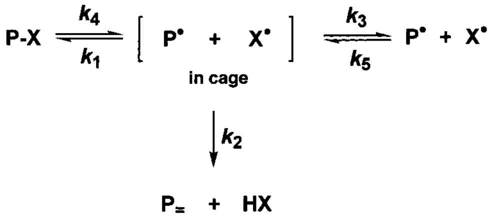
(a) Reversible Activation



(b) Decomposition



Scheme 2. Mechanistic Scheme of Bimolecular Decomposition in the Cage of Solvent



Experimental Section

Materials. DEPN was prepared according to the procedure of Tordo et al.[4] 1-Phenylethyl (S) and *tert*-butoxycarbonyl-2-propyl (BMA) nitroxide adducts were prepared according to the procedure of Matyjaszewski et al.[19] All other reagents were commercially obtained and used without further purification.

Determination of k_{act}. An acetonitrile solution of S-TEMPO (4 mM) and HTEMPO (80 mM) was charged in a glass tube, degassed with several freeze–pump–thaw cycles, and sealed off under vacuum, where HTEMPO is 4-hydroxy-TEMPO. The solution was heated at 110–125 °C for a prescribed time *t* and quenched to room temperature. The reaction mixture was then diluted with acetonitrile and analyzed by high-performance liquid chromatography (HPLC). S-HTEMPO (0.1 mM) dissolved in *tert*-butylbenzene was charged in a quartz tube and sealed off in air. The solution was heated in an oil bath at 90–110 °C for a prescribed time *t*, quenched to room temperature, and then analyzed by electron spin resonance (ESR) at room temperature.

Determination of k_{dec}. An alkoxyamine (90 mM) dissolved in toluene-d_8 or acetonitrile-d_3 was charged in a nuclear magnetic resonance (NMR) tube, degassed with several freeze–pump–thaw cycles, and sealed off under vacuum. In the case of BMA–TEMPO measured in air, the toluene-d_8 solution of alkoxyamine (5 mM) was charged in a NMR tube and sealed in air. In all cases, the reaction mixture was heated in an oil bath (at 140 °C for S-nitroxides and at 80 °C for BMA–TEMPO) for a prescribed time *t*, quenched to room temperature, and then analyzed by ^{1}H NMR at room temperature.

Measurements. The HPLC setup consisted of a Tosoh CCPP-M pump, Tosoh gel column Silica-60, and Shodex differential refractometer RI-72. The analysis was made at room temperature, and acetonitrile was used as eluent. The ESR spectra were recorded at room temperature with JEOL JES-TE 200 spectrometer. The measurement was performed with 100 kHz magnetic field modulation at microwave output of 0.1 mW. The system was calibrated with a degassed *tert*-butylbenzene solution of HTEMPO and the fourth line of Mn^{2+} in the ESR marker. The ^{1}H NMR spectra were obtained with a JEOL GSX-300 spectrometer operating at 300 MHz. These spectra were recorded at ambient temperature, with flip angle of 45°, spectral width of 6013 Hz, acquisition time of 5.449 s, and pulse delay of 1.551 s.

Results and Discussion

Determination of k_{act}. We previously determined the k_{act} of polymer–nitroxide adducts (entries 1–3 in Table 1),[9,20] while Fischer et al. measured those of the corresponding low-mass adducts (entries 4–6).[8] The results showed that the open-chain nitroxides DBN and DEPN give larger k_{act} than the less bulky cyclic-chain nitroxide TEMPO, meaning that steric factors are important. Also, DBN gives a larger k_{act} than DEPN although the latter has a much bulkier side group than the former, implying that the electron-withdrawing phosphonate group in DEPN has an important effect on k_{act}. Thus, electronic (polar) factors also make a significant contribution on k_{act}. Comparison of the k_{act} of polymer adducts with that of the low-mass analogues shows that the former is larger than the latter by a factor 2–3, indicating the importance of the effect of chain length or the "polymer effect".

In this work, we additionally determined the k_{act} of S-HTEMPO to examine the effect of hydroxyl group and that of S-TEMPO in acetonitrile to examine the polar effects of solvent. To determine k_{act}, the alkyl radical $R^\bullet$ formed by the activation of R–X was scavenged by oxygen[8,21,22] or a different nitroxide ($X'^\bullet$),[7,22–24] and the decay of the R–X concentration *C* was followed. A large excess of the scavengers were used to prevent the reformation of R–X by cross-combination of the radicals and thus to determine k_{act} in a pseudo-first-order condition.

For S-HTEMPO, oxygen was used as a scavenger of $R^\bullet$, and the released $X^\bullet$ was monitored by ESR. Figure 2 shows the ESR spectra for the nondegassed solution of S-HTEMPO in *tert*-butylbenzene at 120 °C.[25] The intensity of the ESR spectrum increased with *t* at first but became almost constant after 200 min. The plateau value of [$X^\bullet$] (0.098 mM) was close to C_0 (*C* at time 0)

Table 1. Comparison of k_{act}, k_{dec}, and p_{dec} of Alkyl-Nitroxide Adducts

alkoxyamines	solvent for k_{act}	solvent for k_{dec}	$10^3 k_{act}$/s^{-1}	$10^5 k_{dec}$/s^{-1}	$10^3 p_{dec}$	T/°C
1. PS-DBN	styrene[9]		250			140
2. PS-DEPN	styrene[9]		72			140
3. PS-TEMPO	styrene[20]	toluene-d_8[11]	6.2	2.5	4.0	140
4. S-DBN	*tert*-butylbenzene[8]	toluene-d_8	87	75	8.6	140
5. S-DEPN	*tert*-butylbenzene[8]	toluene-d_8	34	5.3	1.6	140
6. S-TEMPO	*tert*-butylbenzene[8]	toluene-d_8	3.8	4.5	12	140
7. S-TEMPO	acetonitrile[a]	acetonitrile-d_3	8.8	10	12	140
8. S-HTEMPO	*tert*-butylbenzene[b]	toluene-d_8	3.3	1.3	3.9	140
9. BMA-TEMPO	*tert*-butylbenzene[8]	toluene-d_8	0.34	1.4	42	80

[a] k_{act}/s^{-1} = 1.2 × 10^{14} exp(−128 kJ mol^{-1}/RT). [b] k_{act}/s^{-1} = 9.7 × 10^{14} exp(−138 kJ mol^{-1}/RT).

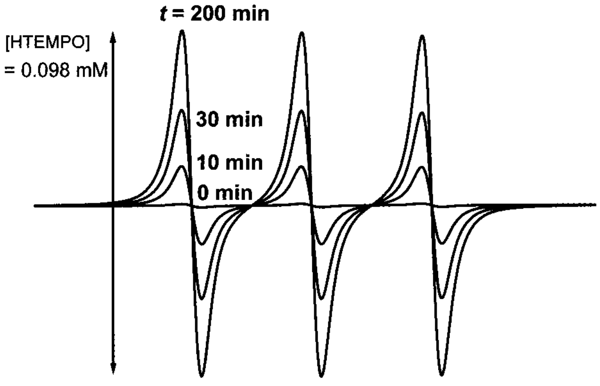


Figure 2. ESR spectra of HTEMPO for the nondegassed solution of S-HTEMPO in *tert*-butylbenzene heated at 120 °C. $[\text{S-HTEMPO}]_0$ = 0.1 mM.

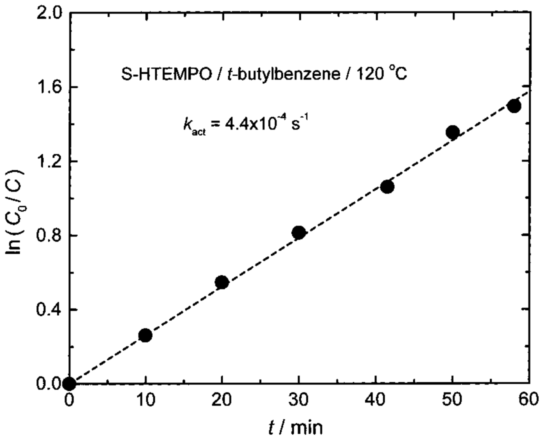


Figure 3. Plot of ln(C_0/C) vs t for the activation of S-HTEMPO in *tert*-butylbenzene at 120 °C. For the experimental conditions, see Figure 2.

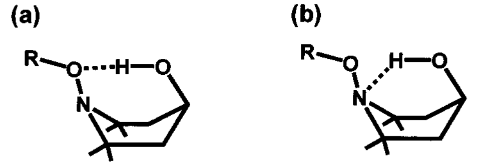


Figure 4. Proposed structures for hydrogen bonding of alkyl-HTEMPO adducts.

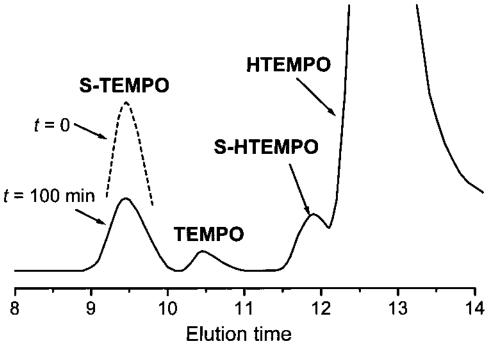


Figure 5. HPLC charts for the degassed solution of S-TEMPO and HTEMPO in acetonitrile heated at 100 °C. $[\text{S-TEMPO}]_0$ = 4 mM and $[\text{HTEMPO}]_0$ = 80 mM.

(0.1 mM), meaning that the increase of [X$^\bullet$] corresponds to the decrease of C. Figure 3 shows the first-order plot of C. The plot is almost linear, and the slope of the straight line gives k_{act}. As a reference, we also determined the k_{act} of S-TEMPO at 120 °C to be 5.7 × 10^{-4} s^{-1}, which well agreed with the value reported by Fischer et al.[8] (5.2 × 10^{-4} s^{-1}). Thus, the k_{act} of S-HTEMPO obtained here can be compared with those due to Fischer et al. For the alkyl-HTEMPO adducts, there has been proposed two structures of intramolecular hydrogen bonding (Figure 4, a[26] and b[27]), and their steric effects on k_{act} have been suggested to be important[27] or unimportant.[26] The present results show that the k_{act} of S-HTEMPO (entry 8 in Table 1) is almost the same as that of S-TEMPO (entry 6). This means that the effect of intramolecular hydrogen bonding on k_{act} is minor in the case of HTEMPO adducts. It should be noted that, however, dramatic effects of hydrogen bonding were observed for some nitroxides with phosphonic acid[26] or tris-hydroxy groups.[28–30]

The k_{act} of S-TEMPO was determined in acetonitrile by using a different nitroxide, HTEMPO, as a scavenger. HPLC was used to follow the concentration of S-TEMPO, which was distinguishable from other species by HPLC. We did not use the ESR method, since polar solvents such as acetonitrile are less suitable for a quantitative analysis by ESR. Figure 5 shows the HPLC chart for the degassed mixture of S-TEMPO, HTEMPO, and acetonitrile heated at 100 °C for 100 min. After the heat treatment, the peaks for TEMPO and S-HTEMPO newly appeared, while that for S-TEMPO became smaller. Figure 6 shows the first-order plot of C, by which k_{act} was obtained. The k_{act} in acetonitrile is larger than that in *tert*-butylbenzene (Table 1), suggesting that the polar effect is important to determine k_{act}, as mentioned above. Such a solvent effect has also been reported for a different alkoxyamine.[2,7]

Determination of k_{dec}. We determined the k_{dec} for the systems 4–9 in Table 1. Figure 7 shows the ^{1}H NMR spectra (in the range of 4.5–6.9 ppm) for the degassed solution of S-TEMPO (90 mM) in toluene-d_8 heated at 140 °C. The signal at 4.8 ppm is assigned to the α-methine proton of S-TEMPO, while those at 5.05, 5.6, and 6.55 ppm correspond to the double-bond protons of the decomposed species, i.e., styrene. The intensities of the signals became smaller for S-TEMPO and larger for styrene as time elapsed, and the peak for the former completely disappeared in 18 h, meaning that the

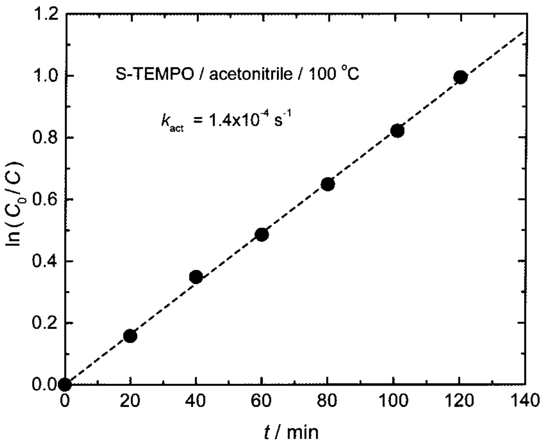


Figure 6. Plot of $\ln(C_0/C)$ vs t for the activation of S-TEMPO in acetonitrile at 100 °C. For the experimental conditions, see Figure 5.

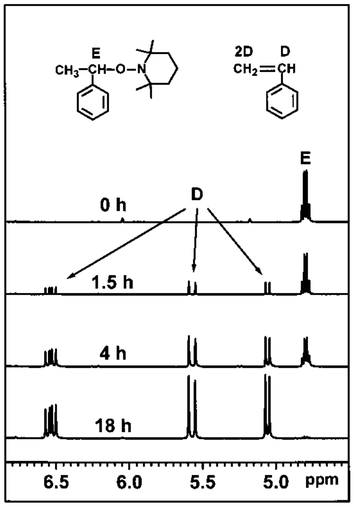


Figure 7. ^{1}H NMR spectra (in the range of 4.5–6.8 ppm) for the degassed solution of S-TEMPO in toluene-d_8 heated at 140 °C. $[\text{S-TEMPO}]_0 = 90$ mM. For the spectrum in the whole range at 4 h, see Supporting Information.

reaction proceeded quantitatively. The concentration D of styrene and that E of S-TEMPO will follow[11]

$$\ln[(E + D)/E] = k_{dec}t \quad (2)$$

since $E + D = E_0$, where E_0 is the initial concentration of S-TEMPO. No signals for 2,3-diphenylbutane, the alkyl dimer species, were detected in this experiment, indicating the unimportance of the alkyl–alkyl termination (Supporting Information).[31] Furthermore, the sum of E and D relative to the concentration (peak intensity) for the methyl protons of undeuterated toluene (at $\delta = 2.1$ ppm) was kept constant, meaning that other side reactions are also negligible. In the case of S-DEPN, we intentionally added extra DEPN (30 mM) to prevent termination,[32] since the equilibrium constant ($K = k_{act}/k_{deact}$) is very large in this system.[6,33] Figure 8 shows the plot of $\ln[(E + D)/E]$ vs t for S-TEMPO at 140 °C, giving a well-defined k_{dec} value. A similar plot was obtained for all other cases with S-nitroxide adducts examined, allowing us to calculate p_{dec} according to eq 1. (For BMA–TEMPO, see below.)

The results for entries 4–6 in Table 1 show that TEMPO, DBN, and DEPN attached to the same alkyl (S–) group give large differences in p_{dec}. The p_{dec} decreases with an increase of the size of nitroxide (TEMPO < DBN < DEPN), indicating a strong steric effect on p_{dec}. The p_{dec} of PS-TEMPO (entry 3) is smaller than that of S-TEMPO (entry 4), even if difference in the number of β-protons (two for PS-TEMPO and three for S-TEMPO) is taken into accounted. This would result from the difference in the size of the alkyl moiety, which again confirms the importance of the steric effect on p_{dec}. The p_{dec} of S-TEMPO in *tert*-butylbenzene (entry 4) coincides with that in acetonitrile (entry 7), suggesting the insignificance of the polar effect on p_{dec}. The hydroxyl group in HTEMPO has no effect on k_{act}, as mentioned above, while it gives an appreciable effect on p_{dec} (entries 4 and 8). The intramolecular hydrogen bonding in a free nitroxide may be stronger than that in an alkoxyamine, since a free nitroxide can take the dipole structure ($^+$N–O$^-$) as a resonance form which would stabilize the hydrogen bonding. The hindered conformation due to the hydrogen bonding could be a reason for the smaller p_{dec} of S-HTEMPO than that of S-TEMPO.

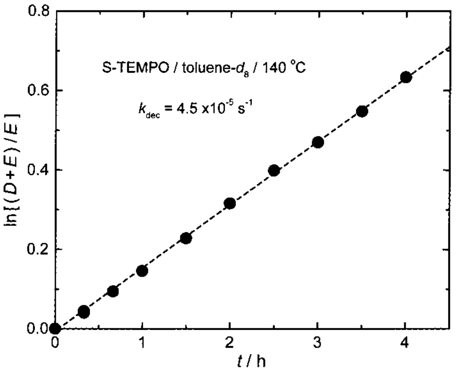


Figure 8. Plot of $\ln[(D + E)/E]$ vs t for the decomposition of S-TEMPO in toluene-d_8 at 140 °C. For the experimental conditions, see Figure 7.

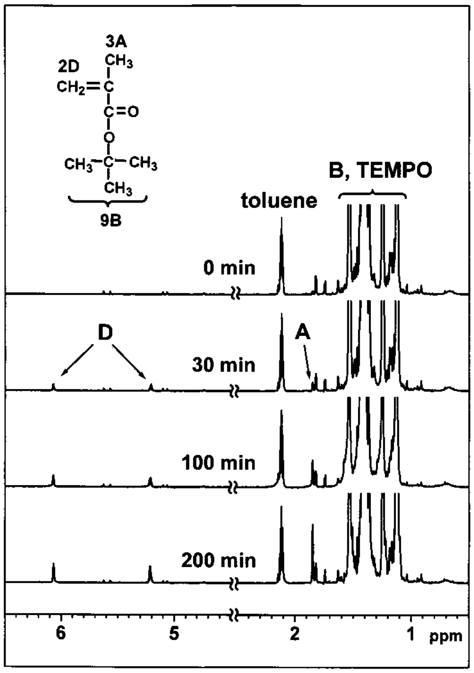


Figure 9. ^{1}H NMR spectra (in the range of 4.5–6.8 ppm) for the degassed solution of BMA–TEMPO in toluene-d_8 heated at 80 °C. $[\text{BMA–TEMPO}]_0 = 90$ mM.

Figure 9 shows the ^{1}H NMR spectra for the degassed solution of BMA–TEMPO (90 mM) in toluene-d_8 heated

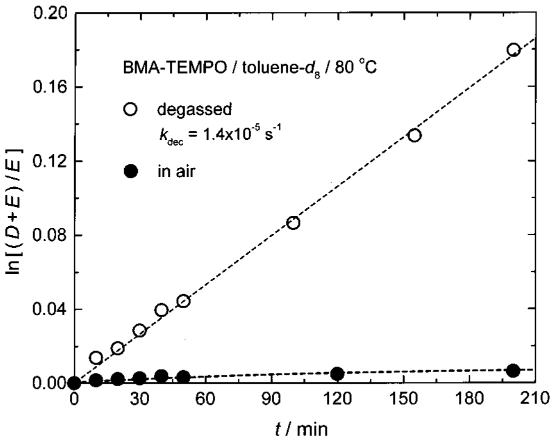


Figure 10. Plot of $\ln[(D + E)/E]$ vs t for the decomposition of BMA−TEMPO in toluene-d_8 at 80 °C. $[\text{BMA−TEMPO}]_0 = 90$ mM without O_2 (○) and $[\text{BMA−TEMPO}]_0 = 1$ mM with O_2 (in air) (●).

at 80 °C. The signals at 5.2 and 6.1 ppm are assigned to the double-bond protons of the decomposed species, i.e., *tert*-butyl methacrylate. The intensity of these signals became larger with t. The absolute concentration D of *tert*-butyl methacrylate at each time was determined from the relative intensity of the peak for the double-bond protons and that for the methyl protons of undeuterated toluene, which is calibrated with the known concentration of *tert*-butyl methacrylate in the same toluene-d_8. The concentration E of BMA−TEMPO can be calculated from $E_0 - D$, and thus eq 2 is also applicable to this case. Figure 10 shows the plot of $\ln[(E + D)/E]$ vs t (open circle), from which k_{dec} could be obtained. The calculated p_{dec} of BMA−TEMPO (entry 9) is, despite the lower temperature of measurement, larger than that of S-TEMPO (entry 4), indicating that the methacrylate polymerization is more vulnerable to decomposition than the styrene polymerization. The p_{dec} value of 0.042 means that a half of alkoxyamine is decomposed in ca. 15 activation−deactivation cycles. This explains why a narrow polydispersity is hardly obtained for TEMPO/methacrylate (and perhaps other nitroxide/methacrylate) systems. According to Fischer et al.,[17] p_{dec} is 0.008 and 0.028 for S-TEMPO and BMA-TEMPO, respectively, in chlorobenzene-d_5 at 100 °C. These values are reasonably close to ours, if the temperature differences are taken into account.

Mechanistic Scheme of Decomposition. As already implied, we assume that decomposition is a bimolecular reaction in the cage of solvent (Scheme 2). The β-H abstraction can occur in both activation and deactivation processes, and thus we here distinguish the k_{dec} in the activation and deactivation processes as k_{dec1} and k_{dec2} and the associated p_{dec} as p_{dec1} and p_{dec2}, respectively ($k_{dec} = k_{dec1} + k_{dec2}$ and $p_{dec} = p_{dec1} + p_{dec2}$). According to Scheme 2, k_{act}, k_{dec1}, and k_{dec2} take the form

$$k_{act} = k_4 f_3 \tag{3}$$

$$k_{dec1} = k_4 f_2 \tag{4}$$

$$\begin{aligned} k_{dec2} &= k_{act} f_2 (1 + f_3 + ... + f_3^{\,n}) \quad (n \rightarrow \infty) \\ &= k_4 f_2\, f_3/(1 - f_3)^{-1} \end{aligned} \tag{5}$$

where $f_i = k_i/(k_1 + k_2 + k_3)$ with $i = 1$, 2, or 3. The term $(1 + f_3 + ... + f_3^{\infty})$ in eq 5 shows the mean number of chances that the once activated P$^\bullet$ encounters an X$^\bullet$ until they recombine or decompose. (The P$^\bullet$ and X$^\bullet$ in the cage can diffuse apart with a probability f_3.) With eqs 3−5, k_{dec} and p_{dec} read

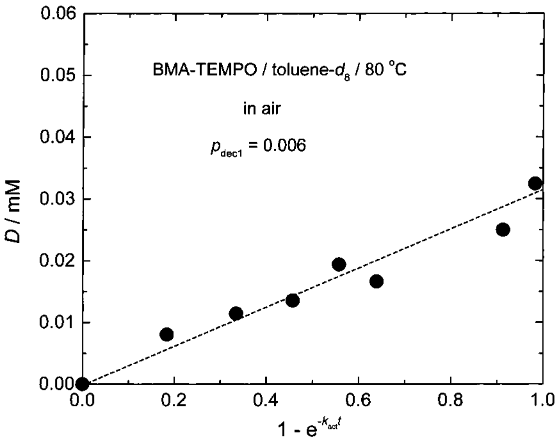


Figure 11. Plot of D vs $1 - \exp(-k_{act}t)$ for the decomposition of BMA−TEMPO in toluene-d_8 in air at 80 °C. $[\text{BMA−TEMPO}]_0 = 1$ mM.

$$k_{dec} = k_4 f_2 + k_4 f_3\, f_2/(1 - f_3) \tag{6}$$

$$p_{dec} = f_2/f_3 + f_2/(1 - f_3) \tag{7}$$

To separate k_{dec} into k_{dec1} and k_{dec2}, we examined the BMA−TEMPO system in the presence of oxygen. As shown above, oxygen can scavenge the alkyl radical, hampering the deactivation process. Figure 10 shows the plot of $\ln[(E + D)/E]$ vs t (open circles) for BMA−TEMPO in air. Apparently, the decomposition rate dramatically decreased in the presence of oxygen. This is ascribed to the decrease of the adduct concentration by the work of oxygen. Since E (the adduct concentration) is given by $E_0 \exp(-k_{act}t)$, the time dependence of D (the concentration of the decomposed species) will take the form

$$dD/dt = k_{dec1}E = k_{dec1}E_0 \exp(-k_{act}t) \tag{8}$$

Integration of eq 8 gives

$$D = p_{dec1}E_0[1 - \exp(-k_{act}t)] \tag{9}$$

Figure 11 shows the plot of D vs $1 - \exp(-k_{act}t)$, giving p_{dec1} to be 0.006. With this and the p_{dec} value of 0.042 (in the absence of oxygen), we obtain $p_{dec2} = 0.036$. These results clearly demonstrate that $p_{dec1} \ll p_{dec2}$ (hence $k_{dec1} \ll k_{dec2}$). This relation should not be special for the BMA−TEMPO system. We believe that the difference in k_{dec1} and k_{dec2} can be even larger for other alkoxyamines, since the k_{deact} for BMA−TEMPO is among the largest in alkoxyamines,[34] and alkoxyamines with smaller k_{deact} would have a larger f_3 and hence a larger k_{dec2}/k_{dec1} $(= f_3/(1 - f_3))$. (The encounter of P$^\bullet$ and X$^\bullet$ is a diffusion-controlled process, and the rate constant k_5 may not largely depend on the kinds of P$^\bullet$ and X$^\bullet$ for small molecules. Since k_{deact} is proportional to $k_5 f_1$, a smaller k_{deact} would mean a smaller f_1 and hence a larger f_3.) With the above values of p_{dec1} and p_{dec2}, we also estimate that $f_1 = 0.14$, $f_2 = 0.005$, and $f_3 = 0.85$.

In the discussion given so far, we have ruled out the possibility of decomposition caused by a unimolecular reaction of P−X including the simultaneous bond cleavage and formation. Scaiano et al.[13] have suggested the importance of this process. However, the present results show that a unimolecular pathway is minor, if any present, and its contribution never exceeds 15% (= $p_{\mathrm{dec1}}/p_{\mathrm{dec}}$) in the BMA−TEMPO system. Fischer et al.[17] made a similar analysis using monomer as a scavenger instead of oxygen used in our experiment, and with the aid of a computer simulation, they reached a qualitatively similar conclusion. These authors, however, suggest the importance of the unimolecular pathway for the acrylate/TEMPO system.[17]

Conclusions

The k_{act} and k_{dec} were determined in some nitroxide systems. It was previously demonstrated[7−9] that both steric and polar factors associated with the structure of nitroxides strongly affect k_{act}. Namely, nitroxides with a bulky and electron-donating substituent give higher activation rates. The chain length of the alkyl moiety has also an important effect on k_{act} due to the steric factor. This work has added the observation that k_{act} is affected by solvent polarity. On the other hand, the hydroxyl group in HTEMPO has no effect on k_{act}. Decomposition was found to be dominated by steric factors rather than polar ones. Bulky substituents in nitroxides more effectively prevent decomposition probably due to the highly crowded transition state in this reaction. The polymer effect is important in decomposition, too, which again confirms the importance of the steric factor in decomposition. The hydroxyl group in HTEMPO has a significant effect on decomposition but not on activation. Mechanistically, decomposition is a bimolecular reaction (with only a minor contribution from the unimolecular pathway, if any). The chance of decomposition is larger at the deactivation process than at the activation process.

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Supporting Information Available: ^{1}H NMR spectrum (in the whole range) for the degassed solution of S-TEMPO in toluene-d_8 heated at 140 °C for 4 h: [S-TEMPO]$_0$ = 90 mM, the signals of methine protons of 2,3-diphyenelbutane, if any present, appearing at 2.65 and 2.75 ppm. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(31) In the heat treatment of an alkoxyamine with no extra nitroxide added and no conventional initiation, it holds that $[\mathrm{X}^\bullet]^3 = 3k_t(KE_0)^2t$, where k_t is the termination rate constant and K is the equilibrium constant (= $k_{\mathrm{act}}/k_{\mathrm{deact}}$).[35−37] With the known values of $k_{\mathrm{act}} = 3.8 \times 10^{-3}$ s^{-1},[8] $k_{\mathrm{deact}} \approx 2.5 \times 10^8$ M^{-1} s^{-1},[34] $k_t \approx 1.9 \times 10^9$ M^{-1} s^{-1},[34] and $E_0 = 0.090$ M; $[\mathrm{X}^\bullet]$ at 4 h (at the end of the measurement (Figure 8)) is estimated to be 5.3×10^{-4} M, which corresponds to the amount of the dimer species. This figure means that only ca. 0.6% of S-TEMPO was converted to the dimer species in 4 h, justifying the observation that the signal for dimer species was too small to be detected (Supporting Information).

(32) Without an extra nitroxide, a large K results in a large amount of the dimer species (see above[31]).

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