Factors Influencing the C−O−Bond Homolysis of Trialkylhydroxylamines

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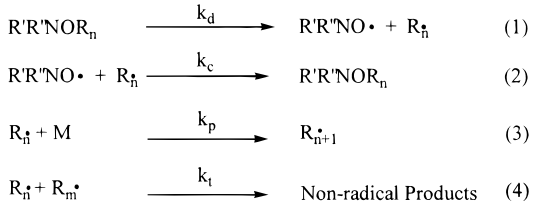
ABSTRACT: Trialkylhydroxylamines and persistent nitroxide radicals are important regulators of living radical polymerizations. Since the polymerization times decrease with increasing rate of the C−O-bond dissociation between the polymer chain and the nitroxide moiety, the factors influencing the homolysis rate constants are of considerable interest. Here, data are presented for 27 model trialkylhydroxylamines in solution containing TMIO, TEMPO, TEDIO, TIPNO, DBNO, SG1, and similar nitroxide groups and primary, secondary and tertiary carbon-centered leaving radicals R. On the average, the frequency factor is $A = 2.6 \times 10^{14}$ s^{-1}, and the activation energies reveal steric effects of both the radical and the nitroxide substituents. Moreover, they increase strongly with increasing C−H-bond energy of the corresponding R−H compounds, and for the same R, decrease in the order TMIO > TEMPO > TIPNO > TEDIO > SG1 ≈ DBNO. The rate constants agree well with data reported for polymerizing systems, and increments are given for radical and nitroxide substitutions which should facilitate predictions for other alkoxyamines.

Introduction

Following the seminal work of Rizzardo et al.,[1] many groups of authors[2] have shown that trialkylhydroxylamines (alkoxyamines) are able to mediate living radical polymerizations of some vinyl monomers. This yields polymers with adjustable molecular weight, low polydispersity, and reactive nitroxide end groups, which allow chain extensions and the development of new block-copolymer architectures. The simplest mechanism involves the reversible dissociation of a dormant nitroxide capped polymer chain with $n \geq 0$ monomer units into a transient carbon-centered radical $R_n^\bullet$ and a persistent nitroxide radical (reactions 1 and 2 in Scheme 1), the propagation of the carbon-centered radical (reaction 3) and its irreversible termination (reaction 4) and exhibits the so-called persistent radical effect.[3] In short, reaction 1 produces the transient carbon-centered and persistent nitroxide radicals in equal amounts. By reaction 2, they react back to the alkoxyamine, also in equal amounts. In addition, the unavoidable irreversible termination reaction 4 diminishes the concentration of the transient species. This leads to unequal radical concentrations and a build-up of excess persistent nitroxide as time proceeds. Consequently, the rate of reaction 2 increases with time, and this reaction then dominates over reaction 4. In the course of time a quasi-equilibrium of the reversible dissociation steps (reactions 1 and 2) is reached. It is unusual because there is a large excess of the persistent species and because both radical concentrations are weakly time-dependent. If this quasi-equilibrium is rapidly established in comparison to the monomer conversion, all chains grow uniformly from $n = 0$ on. The same principle holds for the so-called atom transfer radical polymerization (ATRP).[4]

Scheme 1



A kinetic treatment[5] with chain-length independent rate constants has shown that the polymerization time decreases with increasing equilibrium constant $K = k_d/k_c$ of the reversible dissociation of the nitroxide-capped polymer alkoxyamine. That is, it decreases with increasing k_d. The polydispersity decreases with increasing conversion and becomes small for large products $k_d k_c$. In successful living radical polymerizations, k_d is sufficiently large to ensure reasonable conversion times and low polydispersities. However, k_d must not exceed a critical value for which the controlling persistent radical effect breaks down, and the optimum values for k_d and k_c depend on the propagation and termination rate constants. As a rule, $k_d \geq 10^{-3}$ s^{-1} is desirable, and it would be helpful if k_d could be reasonably predicted based on alkoxyamine and nitroxide structure to avoid unnecessary synthetic and experimental work. For selected cases, the enthalpic and steric factors that influence the dissociation rate constants have been addressed before,[6−12] although there are not yet enough data to make predictions.

To partly fill this gap, we present rate constants for the dissociation of a large variety of low molecular model alkoxyamines with representative substitutions of the nitroxide and the alkyl moiety. We also present their Arrhenius parameters in *tert*-butylbenzene as an inert solvent, and analyze all available data. The results for low molecular weight leaving radicals in the absence of monomer should also approximate polymerizing sys-

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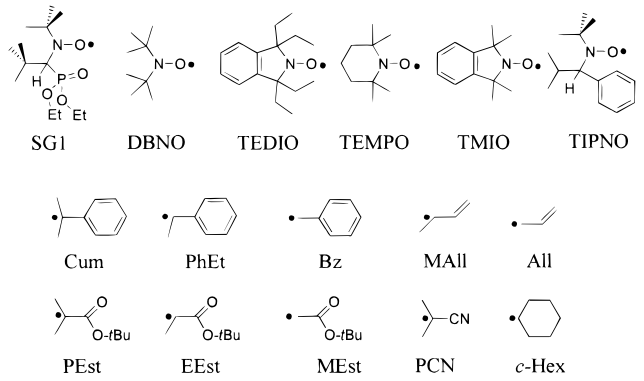
Scheme 2



tems with similarly substituted propagating radicals. Since there is no propagation in the present case and $n = 0$, only reactions 1, 2, and 4 should occur. Reformation of the alkoxyamine by reaction 2 increases its apparent lifetime considerably.[3,5,13] Therefore, k_d cannot be taken directly from its decay under normal reaction conditions. Instead, conditions have to be chosen such that the transient radicals are rapidly and completely converted to other unreactive species before reaction 2 can occur. The increased lifetime has been noticed in early work[6−8] from the fact that the alkoxyamine decay rates increase in the presence of the radical traps I_2, oxygen, and nitroso compounds. Other authors employed different nitroxides, styrene, or good hydrogen atom donors to prevent the back-reaction.[9−12] In our earlier work,[13] we have shown that k_d can be measured conveniently by quantitative CW−ESR spectroscopy from the appearance of the nitroxide radical using the commercially available galvinoxyl radical (2,6-di-*tert*-butyl-4-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidenmethyl)phenoxyl) as a scavenger for the transient radicals. This is used here again, in addition to oxygen (air) and a specially labeled nitroxide. Recently, a related ESR-study with oxygen as trapping agent has also become available.[14]

Scheme 2 shows the nitroxide and alkyl parts of the alkoxyamines. In particular, the nitroxides are *N*-(2-methylpropyl)-*N*-(1-diethylphosphophono-2,2-dimethylpropyl)-*N*-oxyl (SG1, a designation pointing to the name of the inventor) and some related compounds, di-*tert*-butylnitroxyl (DBNO), 2,2,10,10-tetraethylisoindolin-*N*-oxyl (TEDIO), 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO), 2,2,10,10-tetramethylisoindolin-*N*-oxyl (TMIO) and 2,2,5,5-tetramethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO). The leaving radicals are R = cumyl (Cum), phenylethyl (PhEt), benzyl (Bz), butene-3-yl (MAll), allyl (All), 2-*tert*-butoxycarbonyl-2-propyl (PEst), 1-*tert*-butoxycarbonylethyl (EEst), *tert*-butoxycarbonylmethyl (MEst), 2-cyano-2-propyl (PCN), and cyclohexyl (*c*-Hex). However, all derivatives were not available for all nitroxides. PhEt should be a reasonable model for the propagating radical of styrene, Cum for α-methylstyrene, EEst for acrylates, PEst for methacrylates, and PCN for methacrylonitrile.

Experimental Section

Materials. The TEMPO and DBNO derivatives were synthesized following known procedures[15] and were purified by recrystallization or Kugelrohr distillation (typically, $T = 40-50$ °C at 10^{-4} mbar). The procedures for the synthesis of SG1 derivatives and related compounds such as TIPNO−PhEt have also been described earlier.[15] A sample of TIPNO−PhEt with a different diastereoisomer ratio was also received from R. Braslau, University of California at Santa Cruz.[16] TMIO−$^{15}ND_{12}$ (less than 0.1% of unlabeled TMIO by ESR) was obtained from CEA France. TMIO−PCN, TEDIO−PCN, and the allylic TEMPO derivatives came from Ciba Specialty Chemicals.

All alkoxyamines were stored at −20 °C and had purities larger than 98% (NMR) and the expected NMR spectra. TEMPO (Aldrich) was sublimed (97% pure by titration). Galvinoxyl (Aldrich, purity 96% by titration, mp = 158.5 °C, lit.[17] mp = 157.5 °C) and DBNO (90%, Aldrich) were used as received. The solvent *tert*-butylbenzene was purified by standard procedures (distillation, washing with concentrated H_2SO_4, neutralization, drying over $CaCl_2$, vacuum distillation over Na, storage over activated molecular sieves).

Almost all of the alkoxyamines are stable in solution for only a few hours and develop traces of nitroxide contamination, even at −20 °C. The DBNO derivatives are oils and decompose slowly. Consequently, all samples were freshly prepared from pure compounds, and the DBNO derivatives were used immediately after distillation.

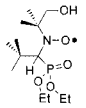
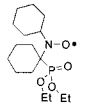
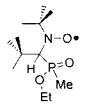
ESR Measurements. The time evolution of the doubly integrated ESR signal of the nitroxide radicals was followed by CW−ESR spectroscopy (Bruker ER 100E) with samples deoxygenated by several freeze−pump−thaw cycles and sealed under helium. Samples with oxygen (air) as scavenger were only sealed. Samples with known concentrations of the persistent nitroxide radicals served as calibration standards.

The appearance of the nitroxides was followed in *tert*-butylbenzene (0.6 mL) containing initially typically 0.1 mM of the trialkylhydroxylamine and a large excess of the scavengers galvinoxyl (5 mM), TMIO−$^{15}ND_{12}$ (1 mM), or air. For TEMPO−Cum, we noted previously that the rate of TEMPO appearance increased with increasing galvinoxyl concentration when the galvinoxyl excess ratio was less that 25:1.[13] Since the determination of the true unimolecular decay rate constant k_d from the rate of nitroxide appearance requires a zeroth order dependence on the scavenger concentration, i.e., saturation conditions, it was ensured in the present study that a large scavenger excess sufficient for saturation conditions was always used. Also, we ensured by experiments with pure oxygen that the oxygen concentration in the air-saturated samples led to complete scavenging.

Furthermore, the appearance of the nitroxide radical will correctly reflect the alkoxyamine decomposition only if the nitroxide and the scavenger radicals are stable on the time scale of the measurement. Therefore, their half-lives were determined separately at 120 °C under experimental conditions equivalent to those of the kinetic runs. As shown in Table 1, the half-lives of the nitroxides are fairly long and are affected by slight impurities, and they varied significantly with sample preparation. Hence, they represent rough values only. In the presence or absence of air[18] and of TMIO−$^{15}ND_{12}$ most nitroxides are stable for several hours, and decay mechanisms are available.[19] They are less stable in the presence of excess galvinoxyl. Further, galvinoxyl decays relatively fast (5 mM, 120 °C, $t_{1/2} = 5.9$ h) at temperatures above 100 °C,[17] but this did not disturb the observed decay of most alkoxyamines because the scavenger was applied in sufficiently large excess.

Figure 1a shows an ESR spectrum taken during the decomposition of TEMPO−Cum in the presence of galvinoxyl. The galvinoxyl lines cover about 15 G of the center of the spectrum, but the low field lines of ^{14}N-TEMPO or other ^{14}N-nitroxides are not distorted and these low field lines were followed for analysis. TMIO−$^{15}ND_{12}$ shows a doublet with $a_N = 20$ G which leaves the center line of ^{14}N-TEMPO from the decomposition of TEMPO−PhEt free for observation, at least for TMIO concentrations not exceeding 1 mM (Figure 1b). In most cases, the build-up of the nitroxide radical could be monitored until the expected concentration for 100% conversion was approached (Figure 2). The build-up was well represented by the expected first-order kinetics, and the decay rate constants were extracted from plots corresponding to eq 5. Figure 3 shows one example.

Table 1. Half-Lives of Nitroxide Radicals (10^{-4} M) at 120 °C

Nitroxide	Scavenger[a]	$t_{1/2}$ (h)	Comments
TMIO	none	>> 40	
	galvinoxyl	27	First order decay
TEMPO	none	>> 15	
	air	>> 15	
	TMIO-$^{15}ND_{12}$[b]	>> 40	
	galvinoxyl	2.0	
SG1	none	15	First order decay
	air	17	First order decay
	TMIO-$^{15}ND_{12}$[b]	12	First order decay
	galvinoxyl	23	First order decay
TIPNO	none	11	First order decay
	air	[c]	First order decay
	TMIO-$^{15}ND_{12}$[b]	4	95% decay in 12 h at 120°C
	galvinoxyl	2	
	none	8	First order decay. A second nitroxide bearing a phosphorus grows in
	air	16	First order decay
	TMIO-$^{15}ND_{12}$[b]	2	Decay nearly complete in 5.5 h
DBNO	none	3	
	air	5	First order decay
	TMIO-$^{15}ND_{12}$[b]	6	First order decay
	galvinoxyl	4	First order decay
	none	1	Decay nearly complete in 4 h
	air	4	First order decay.
	TMIO-$^{15}ND_{12}$	0.5	Complete decay in 1.5 h
	none	0.5	
	air	0.8	First order decay
	TMIO-$^{15}ND_{12}$	0.3	

[a] None: Degassed solution. Radical scavenger:nitroxide ratio = 50:1. [b] Radical scavenger:nitroxide ratio = 10:1. [c] Three measurements gave half-lifes of 4, 6, and 8 h, respectively.

$$\ln\left(\frac{[\text{nitroxide}]_\infty - [\text{nitroxide}]_t}{[\text{nitroxide}]_\infty}\right) = -k_d t \qquad (5)$$

This procedure could not be applied with galvinoxyl as scavenger for alkoxyamines which decayed in reasonable times only at temperatures above 110 °C because galvinoxyl is not sufficiently stable under these conditions. In that case, either air or TMIO−$^{15}ND_{12}$ was used. Further, when k_d was very small ($\leq 10^{-4}$ s^{-1}) and/or when the appearing nitroxide decayed significantly during the observation time (Table 1), the initial slope of the signal rise at less than 20% conversion was evaluated according to eq 6 (Figure 4), with the theoretical nitroxide signal at infinite time taken from the calibration.

$$[\text{nitroxide}]_t/[\text{nitroxide}]_\infty = k_d t \qquad (6)$$

This method was employed for TIPNO, SG1, and DBNO derivatives below 120 °C and for some TEMPO derivatives. In several cases the validity of the procedures was checked by using two or three different scavengers and the two different evaluation procedures with the same alkoxyamine. The results are presented in Table 2 and show a very reasonable agreement of the different procedures. TEMPO−Bz at 130 °C with galvinoxyl as scavenger is an exception. The rate constant appears to be too low which is attributed to the appreciable decay of galvinoxyl at this high temperature.

A remaining source of error is the formation of nitroxide radicals by oxidation of the product hydroxylamine. This product could be formed under our scavenging conditions from a geminate (cage) hydrogen transfer (disproportionation) reaction of the nitroxide/carbon-radical pair which accompanies the alkoxyamine cleavage in (1). Such a cage reaction has been postulated,[20] and the hydrogen abstraction from hydroxylamines by peroxyl, alkoxyl, phenoxyl, and nitroxide radicals is also known.[19,21] However, with galvinoxyl as scavenger, only traces of hydroxylamine were detected during the homolysis

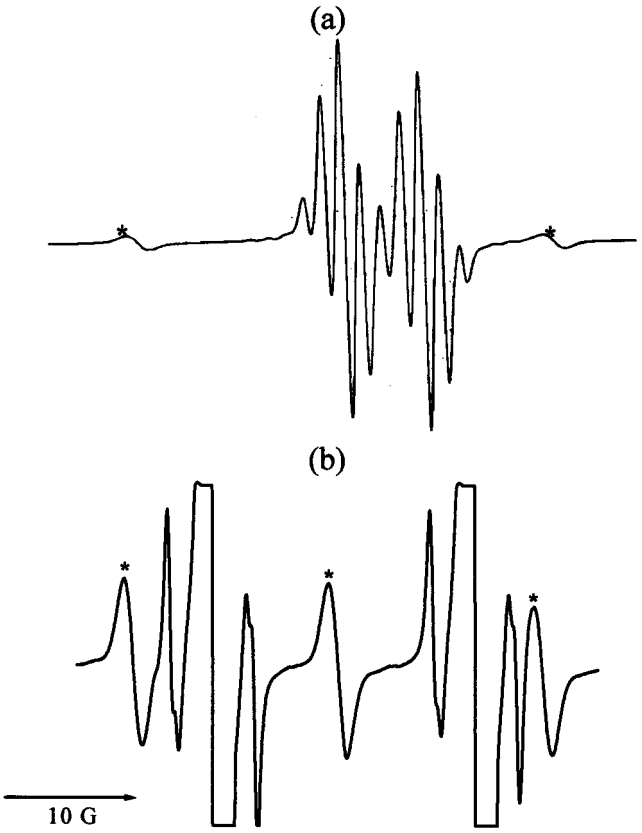


Figure 1. (a) ESR spectrum taken during the decomposition of TEMPO−Cum (1 mM) in the presence of galvinoxyl (5 mM) as scavenger. (b) ESR spectrum taken during the decomposition of TEMPO−PhEt (0.1 mM) in the presence of TMIO−$^{15}ND_{12}$ (1 mM). Kinetic runs with galvinoxyl used a larger scavenger excess.

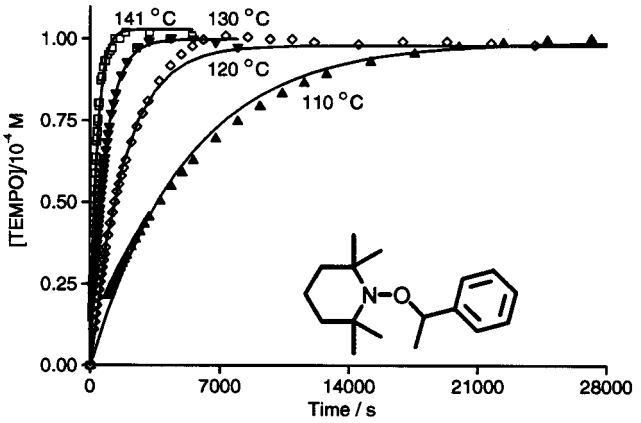


Figure 2. Time dependence of the TEMPO concentration during thermolysis of TEMPO−PhEt in the presence of excess scavengers: 141 °C, galvinoxyl; 130, 120, and 110 °C, TMIO−$^{15}ND_{12}$. Lines are fits of eq 5 to the data.

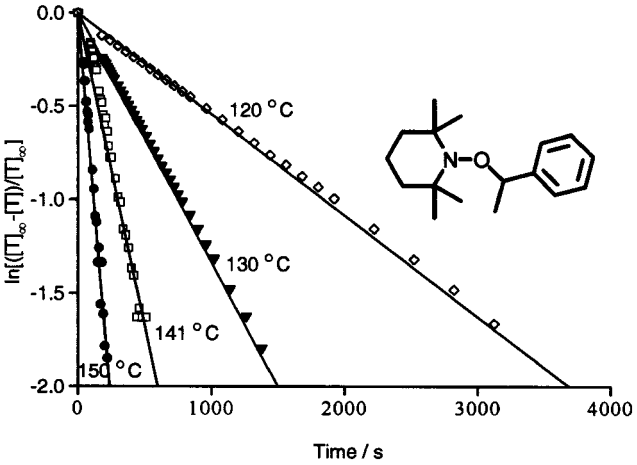


Figure 3. First-order plot (data partially shown in Figure 2) according to eq 5.

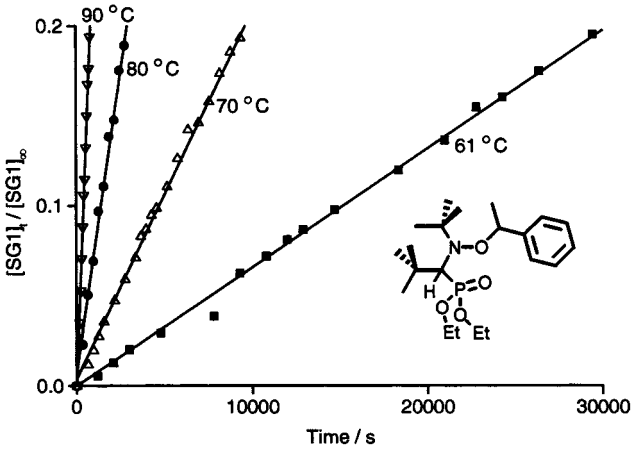


Figure 4. Time dependence of the SG1 concentration during the thermolysis of SG1−PhEt in the presence of excess scavengers: 90, 70, and 61 °C, galvinoxyl; 80 °C, TMIO−$^{15}ND_{12}$. Lines are fits of eq 6 to the data.

of TEMPO−Cum at 80 °C by GC and NMR.[13] Also, in this work no hydroxylamine was detected during the homolysis of TEMPO−PhEt in the presence of TMIO−$^{15}ND_{12}$. On the other hand, in the absence of scavengers and oxidizing species, the decomposition of alkoxyamines leads to hydroxylamines that are easily detected by GC and NMR.[22] These observations suggest that normally the hydroxylamines are formed by the disproportionation between the nitroxide and the carbon-centered radical which competes with the coupling reaction 2 and is likewise quenched under the scavenging conditions. Hence, large cage effects following the dissociation in (1) appear very improbable, which implies a high initiator efficiency of the alkoxyamines.

Results and Discussion

The temperature dependence of k_d was measured for 15 trialkylhydroxylamines, and one example is displayed in Figure 5. The decay of 12 additional trialkylhydroxylamines could only be followed at a few temperatures. All results are collected in Table 3.

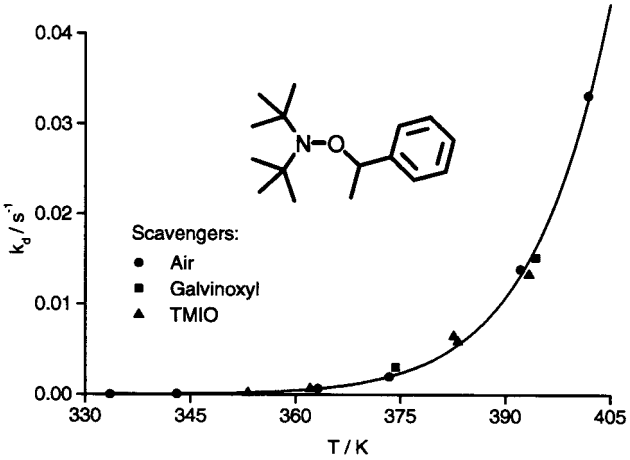


Figure 5. Temperature dependence of the C−O-bond homolysis rate constant of DBNO−PhEt.

Within the error limits the two diastereoisomers of SG1−PhEt showed the same decay constants. The same was found for the two available samples of TIPNO−PhEt with different diastereoisomer composition. One pure diastereoisomer of SG1−EEst and a mixture which contained less than 10% of the pure isomer were also investigated. The rate constant found for the mixture was three times smaller than that of the pure isomer. Hence, in this case the two diastereoisomers exhibit different rate constants, and the same is true for the alkoxyamine in the last entry of Table 3. Furthermore, an approximately 1:1 mixture of the SG1−1-cyanoethyl diastereoisomers showed a double-exponential increase of the nitroxide concentration which was not analyzed in detail. In general, however, the difference of the cleavage rates of different stereoisomers seems to be rather small.

As seen in Table 3, the rate constants obtained at or extrapolated to 120 °C vary with the structure of the alkoxyamine by many orders of magnitude (10^{-8} to 10^{-1} s^{-1}). As far as direct comparisons are possible, our rate constants agree very well with earlier values,[7,9,10,12] and this is also true for the decomposition of a derivative of PhEt−TEMPO in which one methyl hydrogen atom is replaced by a *tert*-butoxy group.[14] The individual activation energies and frequency factors are somewhat different from the earlier data. This may be due to the well-known and unavoidable error compensation effect of the activation parameters which may have affected the analysis both of our and the previous data.

So far, only a few dissociation constants of polymeric alkoxyamines are known. For TEMPO−polystyrene, Fukuda et al.[11] report $k_{393} = 9.9 \times 10^{-4}$ s^{-1}, $A = 3.0 \times 10^{13}$ s^{-1}, and $E_a = 124.0$ kJ mol^{-1}, and Bon et al.[14] find $A = 1.1 \times 10^{16}$ s^{-1} and $E_a = 140.9$ kJ mol^{-1} from which one calculates $k_{393} = 1.9 \times 10^{-3}$ s^{-1}. The rate constants

Table 2. C−O Bond Homolysis Rate Constants of Alkoxyamines (10^{-4} M) Obtained with Different Scavengers

	k_d/s^{-1}				
scavenger	TEMPO−Cum 90 °C	TEMPO−PhEt 140 °C	TEMPO−Bz 130 °C	SG1−PhEt 110 °C	DBNO−PEst 80 °C
galvinoxyl	4.3×10^{-3} [a]	3.3×10^{-3}	2.1×10^{-5} [b]	2.3×10^{-3} [b]	7.6×10^{-3}
TMIO−$^{15}ND_{12}$	5.3×10^{-3}	3.7×10^{-3}	4.0×10^{-5} [b]	2.5×10^{-3}	7.2×10^{-3}
air	7.0×10^{-3} [c]	3.8×10^{-3}			7.1×10^{-3}

[a] [TEMPO−Cum] = 2×10^{-3} M. [b] Calculated with eq 6. [c] 93 °C.

Table 3. Activation Parameters and Rate Constants at 120 °C for the Dissociation of Trialkylhydroxylamines

Alkoxyamine		Runs	T (°C)	A (10^{14} s^{-1})[a]	E_a (kJ mol^{-1})[b]	k_{393} (s^{-1})	Ref.
TMIO-	PCN	9	80 - 120 60	2.7 (2.6)	121.6 122.7	$1.9\cdot10^{-2}$ $1.3\cdot10^{-2}$	9
TEMPO-	Cum	9[c]	70 - 92 35- 75 60	2.0[d] 1.0 (2.6)	115.7 113.7 117.8	$8.5\cdot10^{-2}$ $7.8\cdot10^{-2}$ $5.8\cdot10^{-2}$	10 7
	PCN	15	51- 103 60	6.8 (2.6)	118.4 115.8	0.13 0.11	9
	PEst	16	65 - 121	1.8	119.8	$2.2\cdot10^{-2}$	
	MAll	3	101 - 131	(2.6)	126.7	$3.8\cdot10^{-3}$	
	PhEt	17 9	90 - 150 75 - 120	2.5 0.5	133.0 128.3	$5.2\cdot10^{-4}$ $4.5\cdot10^{-4}$	10
	EEst	11	90 - 151	1.0	139.0	$3.4\cdot10^{-5}$	
	c-Hex	1[e] 2	150 215 - 222	(2.6) 1.25	> 165.3 171.4	$< 2.8\cdot10^{-8}$ $2.1\cdot10^{-9}$	12
	All	2	109 - 130	(2.6)	139.5	$7.5\cdot10^{-5}$	
	Bz	2 9	131 - 150 83 - 154	(2.6) 0.4	145.7 136.3	$1.1\cdot10^{-5}$ $3.1\cdot10^{-5}$	10
	MEst	2	151	(2.6)	161.8	$8.1\cdot10^{-8}$	
TIPNO-	PhEt	10[f]	60 - 131	5.6	129.6	$3.3\cdot10^{-3}$	
TEDIO-	PCN	15	55 - 90 60	1.3 (2.6)	112.1 114.0	0.16 0.18	9
	PhEt	3[g]	101 - 121	(2.6)	126.6	$3.9\cdot10^{-3}$	
	PhEt	13[h]	60 - 131	2.9	126.2	$4.9\cdot10^{-3}$	
SG1-	PhEt 2 isomers	20[h]	60 - 137	1.9	124.5	$5.5\cdot10^{-3}$	
	EEst isomer 1	12[h,i]	80 - 132	3.5	128.4	$3.0\cdot10^{-3}$	
	EEst isomer 2	4[h,i]	90 - 129	(2.6)	130.9	$1.0\cdot10^{-3}$	
	Bz	3[h]	110 - 131	(2.6)	134.6	$3.3\cdot10^{-4}$	
DBNO-	PEst	20	70 - 110	1.0	109.2	0.31	
	PhEt	13	60 - 129 80	2.2 (2.6)	121.8 123.0	$1.4\cdot10^{-2}$ $1.2\cdot10^{-2}$	9,j
	EEst	13	70 - 150	1.2	128.2	$1.1\cdot10^{-3}$	
	Bz	3	110 - 131	(2.6)	136.4	$1.9\cdot10^{-4}$	
	PhEt	3[k]	90 - 120	(2.6)	121.3	$2.0\cdot10^{-2}$	
	PhEt	11[h,l]	60 - 119	0.5	115.0	$2.6\cdot10^{-2}$	
	PhEt S-R-isomer	3[g]	80 -121	(2.6)	118.5	$4.6\cdot10^{-2}$	
	PhEt R-R-isomer	3[g]	80 - 100	(2.6)	116.9	$7.5\cdot10^{-2}$	

[a] Statistical errors smaller than a factor of 2. Value in brackets is the average of all experimentally accessible frequency factors. [b] Statistical errors between 2 and 3 kJ·mol^{-1}. [c] [alkoxy−amine]/[galvinoxyl] = 1/25. [d] Because of additional experiments the Arrhenius parameters are slightly different from those given in ref 13. [e] 1% conversion and [TEMPO−*c*-Hex] = 10^{-2} M. [f] 2:1 mixture (^{1}H NMR) of diastereoisomers, unimodal decay. For a 55:45 mixture the same rate constants were obtained. [g] SG1 used as standard. [h] [alkoxyamine]/[TMIO−$^{15}ND_{12}$] = 1/50. [i] Methyl ester. [j] CH_2O-*t*-Bu instead of CH_3 group. [k] 70:30 mixture (^{1}H NMR) of diastereoisomers, unimodal decay. [l] One diastereoisomer of unknown configuration.

are rather close to those found here for the model compound TEMPO−PhEt ($k_{393} = 5.0 \times 10^{-4}$ s^{-1}) whereas the activation parameters may again suffer from the error compensation effect. Moreover, the two to 4-fold larger values for the polymeric alkoxyamine seem reasonable in view of the larger steric strain on the breaking bond. For SG1−polystyrene, Gnanou et al.[23] determined $A = 10^{14}$ s^{-1} and $E_a = 121$ kJ mol^{-1} ($k_{393} = 3.4 \times 10^{-3}$ s^{-1}) which are similar to our data for SG1−PhEt (Table 3), and the same authors found $A = 1.3 \times 10^{15}$ s^{-1} and $E_a = 130$ kJ mol^{-1} ($k_{393} = 8.9 \times 10^{-3}$ s^{-1}) for SG1−poly-*n*-butyl acrylate which should be compared to our data for SG1−EEst ($A = 2.6 \times 10^{14}$ s^{-1}, $E_a = 129$ kJ mol^{-1}, $k_{393} = 2 \times 10^{-3}$ s^{-1}, for an average of isomers). Finally, Fukuda et al.[11] report singular rate constants $k_{393} = 10^{-3}$ s^{-1} for DBNO−poly-*tert*-butyl acrylate and $k_{393} = 4.2 \times 10^{-2}$ s^{-1} for DBNO−polystyrene which are close to our $k_{393} = 1.1 \times 10^{-3}$ s^{-1} for DBNO−EEst and $k_{393} = 1.2 \times 10^{-2}$ s^{-1} for DBNO−PhEt. In summary, the dissociation rate constants of polymeric and low molecular systems with similar alkoxyamine substitution seem to differ not more than by a factor of 5 with marginally larger values for the polymeric alkoxyamines. Obviously, they are governed by the same effects.

The large variation of the rate constants is not due to a large variation of the frequency factors because our values center around an average of $A = 2.6 \times 10^{14}$ s^{-1} with deviations up to a factor of 2.5 if one anomalously low value is excluded. They are in the expected range for unimolecular decompositions. Therefore, $A = 2.6 \times 10^{14}$ s^{-1} was used to determine several activation energies from rate constants for cases where extended temperature dependencies were not available.

The activation energies range from about 110 to 170 kJ mol^{-1}, and this spread covers the rate constant variations. The generally high activation energies are as expected for an endothermic dissociation process. The reverse reaction, that is the combination of carbon-centered radicals with nitroxides (eq 2), is usually fast ($k_c > 10^7$ M^{-1} s^{-1}) and shows little temperature dependence.[24] Hence, the activation energies must be close to the NO−C bond dissociation energies. Marsal et al.[25] have recently calculated such energies by density functional theory for several systems which are also investigated here. They found 108 kJ mol^{-1} for TEMPO−Cum, 114.5 kJ mol^{-1} for DBNO−PhEt, 120 kJ mol^{-1} for SG1−PhEt, 130 kJ mol^{-1} for TEMPO−PhEt, 135 kJ mol^{-1} for SG1−Bz, and 144 kJ mol^{-1} for TEMPO−Bz, whereas our activation energies are 115.7, 121.8, 124.5, 133.0, 134.6, and 145.7 kJ mol^{-1}. Considering the unknown but small barrier for the combination reaction, the two data sets agree very well. Earlier AM1 and PM3 calculations for TEMPO−PhEt and DBNO−PhEt[26] gave too small bond dissociation energies.

As is obvious from previous work[7−13] and the data of Table 3, the activation energies of alkoxyamine dissociations depend strongly on the structure of the leaving transient radical and on the structure of the nitroxide. In addition, the rate constants seem to increase slightly with increasing solvent polarity. This is probably due to a larger dipole moment of the transition state than of the alkoxyamine and indicates that the transition state already resembles the newly forming nitroxide radical. For the same reason, the combination of carbon-centered radicals with nitroxides is slower in more polar solvents.[24]

To reach predictive rules for alkoxyamine dissociations, we first address the influence of the structure of the leaving radical on the activation energy and consider only the TEMPO derivatives for which the series of leaving radicals is largest. For different leaving radicals, the activation energy should change because the dissociation energy changes (enthalpy effect), as do the polar and steric effects. Since the cleavage becomes more facile with increasing stability of the leaving radical the activation energy should decrease concomitantly. A rough measure of the radical stability is the bond

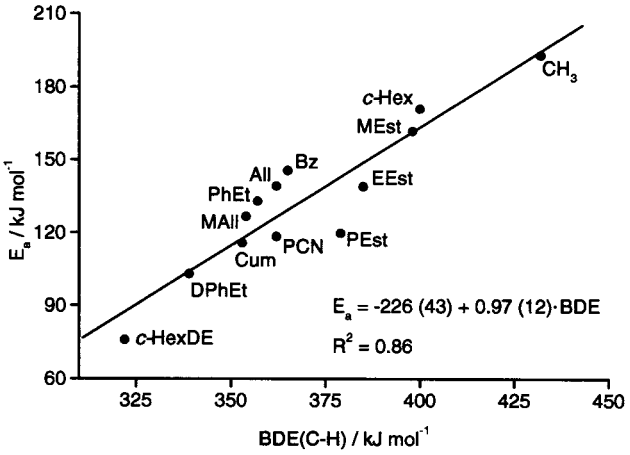


Figure 6. Activation energies E_a for the C−O-bond cleavage of TEMPO-derived trialkylhydroxylamines vs BDE(C−H) of the corresponding hydrocarbons.

dissociation energy BDE(C−H) of the C−H bond of the corresponding alkane. This suggests that a plot of E_a vs BDE(C−H) should show a reasonable correlation.[12] Figure 6 shows a plot constructed from literature or estimated bond dissociation energies BDE(C−H).[27] It includes data reported by Mulder et al.[12] for TEMPO−methyl, −*c*-hexyl, and −*c*-hexadienyl and by Howard et al.[7] for 4-oxo-TEMPO-1,1-diphenylethyl. The very reasonable linear correlation between E_a and BDE(C−H) over a large range demonstrates the major influence of the reaction enthalpy. Our correlation, $E_a = 0.97(12) \times$ BDE(C−H) − 226(43) kJ mol^{-1}, with errors given in the unit of the last quoted digit, agrees well with an earlier correlation of Mulder,[12] which was based on only a few points. Polar effects of the electron-withdrawing carboxy- and cyano-substituents of the leaving radicals seem to be of lower importance than the enthalpy changes.

However, there are considerable steric effects, as is evident from the data for the triples MEst, EEst, PEst, and Bz, PhEt, Cum and for the pair All, MAll. On the average, the introduction of one methyl group in the leaving radical decreases E_a by − (17 ± 4) kJ mol^{-1}, but it decreases the reaction enthalpy (BDE(C−H)) by only − (8 ± 4) kJ mol^{-1}. The activation energies for the tertiary leaving radicals Cum, PCN, and PEst are similar, which means that the steric hindrance precludes the expression of the radical stability effect for the tertiary species more than for the corresponding primary and secondary radicals.

The effects of substitution of the leaving radicals which were found for the TEMPO derivatives are also observed for the derivatives of SG1 and DBNO. Thus, changing from PEst to PhEt changes the activation energy for the TEMPO derivatives by +13.2 kJ mol^{-1} and for the DBNO derivatives by +12.6 kJ mol^{-1}. The change of PhEt to EEst increases E_a by +6.0 kJ mol^{-1} for the TEMPO derivatives, by +3.9 and +6.4 kJ mol^{-1} for the two SG1 diastereomers and by +6.4 kJ mol^{-1} for the DBNO derivatives. The replacement of EEst by Bz yields increases of +6.7 kJ mol^{-1} for the TEMPO, of +6.2 and +3.7 kJ mol^{-1} for the SG1 derivatives, and +8.2 kJ mol^{-1} for the DBNO derivatives. Finally, the exchange of PhEt by Bz gives a change of the activation energy of +12.7 kJ mol^{-1} for the TEMPO derivatives, of +10.1 for the SG1 derivatives, and of +14.6 kJ mol^{-1} for the DBNO derivatives.

Obviously, the increments for alkyl substitutions on the activation energies for the different nitroxide moieties are practically equal within the experimental error limits. Since the frequency factors are all in a narrow range, the common activation energy increments should allow to predict decay constants for alkoxyamine derivatives from the rate constant for one representative sample of a series. Thus, taking the average of the increments for the substitution changes of the activation energies of the TEMPO, SG1, and DBNO derivatives (PEst/PhEt = +12.9, PhEt/EEst = +5.7 and EEst/Bz, = +6.2 kJ mol^{-1}) and the increments for the TEMPO derivatives (Cum/PCN = +2.7, PCN/PEst = +1.4, and Bz/MEst = +16.1 kJ mol^{-1}) we predict the activation energies of other derivatives as listed in Table 4. These yield the predicted rate constants shown in Table 5.

Table 4. Experimental and Estimated[a] Activation Energies (kJ mol^{-1}) for the Dissociation of Trialkylhydroxylamines

	TMIO	TEMPO	TEDIO	TIPNO	SG1	DBNO
Cum−	*118.9*	115.7	*109.4* 116.1[9]	*112.6/112.3*	*107.5/106.1*	*105.1/105.2* 105.5[9]
PCN−	121.6	118.4	112.1	*115.3/115.0*	*110.2/108.8*	*107.8/107.9*
PEst−	*123.0*	119.8	*113.5* 117.5[9]	*116.7/116.4*	*111.6/110.2*	109.2
PhEt−	*135.9/136.2*	133.0	*126.4/126.7*	129.6	124.5	121.8
EEst−	*141.6/142.2*	139.0	*132.1/132.7*	*135.3/135.6*	128.4	128.2
Bz−	*147.8/148.9*	145.7	*138.3/139.4*	*141.5/142.3*	134.6	136.4
MEst−	*163.9/165.0*	161.8	*154.4/155.5*	*157.6/158.4*	*150.7/151.2*	*152.5/151.3*

[a] Estimated activation energies in italics. Where two values are given the first was derived from increments for leaving radicals and the second from increments for nitroxide substitution.

Table 5. Experimental and Estimated[a] Rate Constants (s^{-1}) for the Dissociation of Trialkylhydroxylamines at 120 °C

	TMIO	TEMPO	TEDIO	TIPNO	SG1	DBNO
Cum−	*4.1 × 10^{-2}*	8.5 × 10^{-2}	*0.7*	*0.3*	*1.7*	*2.7*
PCN−	1.9 × 10^{-2}	0.13	0.16	*0.1*	*0.7*	*1.2*
PEst−	*1.2 × 10^{-2}*	2.2 × 10^{-2}	*0.2*	*8.3 × 10^{-2}*	*0.5*	0.31
PhEt−	*2.2 × 10^{-4}*	5.2 × 10^{-4}	*3.9 × 10^{-3}*	3.3 × 10^{-3}	5.5 × 10^{-3}	1.4 × 10^{-2}
EEst−	*3.6 × 10^{-5}*	3.4 × 10^{-5}	*6.6 × 10^{-4}*	*2.5 × 10^{-4}*	3.0 × 10^{-3}	1.1 × 10^{-3}
Bz−	*4.9 × 10^{-6}*	1.1 × 10^{-5}	*9.0 × 10^{-5}*	*3.6 × 10^{-5}*	3.3 × 10^{-4}	1.9 × 10^{-4}
MEst−	*3.5 × 10^{-8}*	8.1 × 10^{-8}	*6.5 × 10^{-7}*	*2.6 × 10^{-7}*	*2.2 × 10^{-6}*	*1.8 × 10^{-6}*

[a] Estimated rate constants in italics, obtained with $A = 2.6 \times 10^{14}$ s^{-1} and the average activation energies of Table 4. The other values are taken from Table 3.

Scheme 3

TMIO	TEMPO	TIPNO	SG1	DBNO
+ 3.2	0	- 3.4	- 9.6	- 10.5 kJ mol^{-1}

Cum	PCN	PEst	PhEt	EEst	Bz
0	+ 2.7	+ 4.1	+ 17.0	+ 22.7	+ 28.9 kJ mol^{-1}

Table 3 also reveals a strong influence of the alkoxyamine nitroxide group. The activation energy for TMIO−PCN is 3.2 kJ mol^{-1} larger than that of TEMPO−PCN, which is 6.3 kJ mol^{-1} larger than that of TEDIO−PCN. The average activation energy difference between the SG1 and TEMPO derivatives is 9.6 (1.5) kJ mol^{-1} (four values), the difference between the DBNO and TEMPO derivatives is 10.5 (1.2) kJ mol^{-1} (four values), and the difference between TIPNO− and TEMPO−PhEt is 3.4 kJ mol^{-1}. As in previous work,[9] the alkoxyamines with open structured nitroxides such as DBNO and SG1 have lower activation energies and decay faster for a given leaving radical than the alkoxyamines with cyclic nitroxides. Within the group of cyclic alkoxyamines with the same substitution at the carbon atoms close to the NO group, the alkoxyamines carrying nitroxides with six-membered rings (TEMPO) decay faster than those with five-membered rings (TMIO). Table 4 also lists values estimated from the average activation energy differences of the alkoxyamines with different nitroxide groups. They agree with those derived from the increments for substitution of the leaving radicals. As a check of the predictive power of the increments, Table 4 also shows activation energies extracted with the common frequency factor of 2.6×10^{14} s^{-1} from alkoxyamine half-lives reported by Moad et al.[9] for TEDIO coupled to radicals derived from α-methylstyrene and methyl methacrylate, and for DBNO coupled to a radical from α-methylstyrene. The similarities of the activation energies of these alkoxyamines and TEDIO−Cum, TEDIO−PEst, and DBNO−Cum supports the preestimation procedure.

Finally, we turn to the influence of the alkyl groups at the carbon atoms bonded to nitrogen in the cyclic alkoxyamines. Comparison of TMIO−PCN and TEDIO−PCN (Table 3) shows that replacement of the four methyl groups by four ethyl groups decreases the activation energy by 9.5 kJ mol^{-1}. This is similar to the decrease by 7.8 kJ mol^{-1} for the replacement of the four methyl groups by four *n*-propyl groups which can be derived from Moad's work.[9] For derivatives resembling TEMPO−Cum and TEMPO−PhEt combination of further data of Moad[9] and of Table 3 yield a decrease of about 5.0 kJ mol^{-1} for the replacement of two methyl groups at different carbon atoms of TEMPO by two *n*-propyl groups. This clearly shows the steric effects of α-substitution at the nitroxide,[9] and the increments given here may again be used for preestimates.

For a better visualization of all these increments, Scheme 3 summarizes the average changes of the activation energies upon replacement of TEMPO by other nitroxides and of the cumyl radical by other carbon-centered radicals.

As pointed out above, satisfactory living radical polymerizations apparently require rate constants for the dissociation of the intermediate polymeric alkoxyamine $k_d \geq 10^{-3}$ s^{-1}. Tables 3 and 5 show such values at 120 °C for TEDIO, TIPNO, SG1, and DBNO derivatives carrying the PhEt residue which resembles the propagation radical of styrene. In fact, styrene polymerizes successfully with TIPNO, SG1, and DBNO derivatives at temperatures close to 120 °C.[2,11,16,23] The decay rate constant of TEMPO−PhEt is borderline. Nevertheless, TEMPO mediates styrene polymerizations very well, but in this case the reaction is accelerated by the styrene self-initiation.[2] The EEst-derived alkoxyamines should reasonably model acrylate polymerizations. TEDIO−EEst and TIPNO−EEst appear also at the borderline, although for TIPNO−EEst[2,16] successful living polymerizations have been reported. SG1[2,23] and DBNO[2,11,28] should and do work with acrylates. Since PEst should model the propagation radical of methyl methacrylate, all alkoxyamines of Table 5 should be able to control the its polymerization. However, success is limited, probably because of a large fraction of disproportionation between the nitroxide and the carbon-centered radical.[22,29]

In total, we expect that our rate constants for low molecular model compounds and the predictive scheme based on them allows to estimate rate constants of the cleavage of large polymeric dormant species within a factor of 10. A favorable decay constant is one prerequisit of a successful living radical polymerization but it is not the only factor because fast processes are also favored by slow cross-combinations (reaction 2). Moreover, in practice, the polymerization rates and the polydispersities are often influenced by the addition of excess nitroxide, extra initiation, the stability of the persistent species, and a variety of possible side reactions so that a favorable decay constant alone will not guaranty success.

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