Polar, Steric, and Stabilization Effects in Alkoxyamines C−ON Bond Homolysis: A Multiparameter Analysis

Denis Bertin, Didier Gigmes, Sylvain R. A. Marque,* and Paul Tordo

UMR 6517 Chimie, Biologie et Radicaux Libres, case 542, Université de Provence, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

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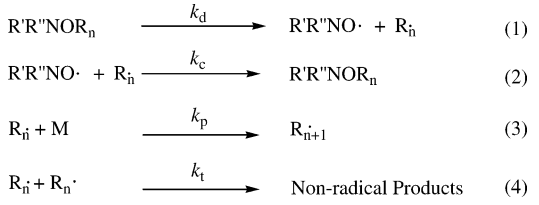
ABSTRACT: We present measurements of the rate constants (k_d) of the C−ON bond cleavage in new alkoxyamine models containing the *N*-(2-methyl-2-propyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1) moiety. The homolysis rate constants of 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)- and SG1-based alkoxyamines are analyzed in terms of polar inductive/field (σ_U), steric (υ), and radical stabilization (σ_{RS}) contributions of the leaving alkyl radicals, using a multiparameter equation, i.e., $\log(k_d/k_{d,0}) = \rho_U\sigma_U + \delta\upsilon + \rho_{RS}\sigma_{RS}$. The rate constants increase with increasing electron withdrawing, steric, and stabilization demands of the leaving alkyl radicals. Good correlations are found for TEMPO ($\log(k_d/k_{d,0}) = 13.6\sigma_U + 6.6\upsilon + 13.9\sigma_{RS}$) and SG1 ($\log(k_d/k_{d,0}) = 19.5\sigma_U + 7.0\upsilon + 15.3\sigma_{RS}$) derivatives, highlighting the polar sensitivity of the leaving alkyl radical to the nitroxyl moiety. Such correlations should facilitate the design of new alkoxyamines as initiators/regulators and help to improve the tuning of NMP experiments.

Introduction

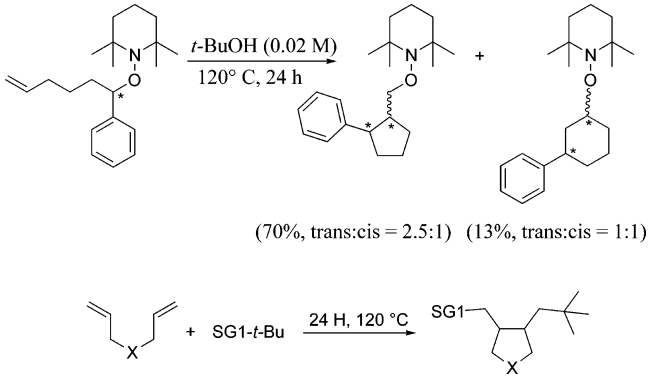
In their seminal works, Rizzardo et al.[1] and later Georges et al.[2] have demonstrated that polymers with polydispersities well below the theoretical limit of 1.5 for classical radical polymerization can be prepared by nitroxide-mediated radical polymerization (NMP). Since then, many groups[3] have pushed this concept further to the preparation of polymers with well-defined architectures, molecular weights, and compositions. These polymerizations are governed by the persistent radical effect (PRE).[4−8] The simplest mechanism involves the reversible dissociation of a dormant nitroxyl end-capped polymer chain with $n \geq 0$ monomer units into a transient carbon-centered radical $R_n^{\bullet}$ and a persistent nitroxyl radical (reactions 1 and 2 in Scheme 1), the propagation of the carbon-centered radical (reaction 3, Scheme 1), and its irreversible termination (reaction 4, Scheme 1).[6]

In the course of time a quasi-equilibrium of the reversible dissociation step (reactions 1 and 2, Scheme 1) is reached. This is unusual because there is a large excess of persistent species and because the two concentrations are weakly time dependent. If this quasi-equilibrium is rapidly established in comparison to the monomer conversion, all of the chains grow uniformly from $n = 0$ on. A kinetic treatment[9] with chain-length-independent rate constants[10] has shown that the polymerization time decreases with increasing equilibrium constants $K = k_d/k_c$ of the reversible dissociation of the nitroxyl end-capped polymer alkoxyamine. That is, it decreases with increasing values of k_d. The polydispersity index decreases with increasing conversion and becomes small for large products k_dk_c. However, k_d must not exceed a critical value for which the controlling PRE breaks down, and the optimum values of k_d and k_c depend on the propagation and termination rate constants (reactions 3 and 4, Scheme 1). In general, $k_d \geq 10^{-3}$ s^{-1} is desirable,[11] and it would be helpful if k_d could be reasonably predicted on the basis of alkoxyamine and nitroxyl radical structures to avoid unnecessary synthetic and polymerization works.

Scheme 1



Scheme 2. Radical Cyclization Reaction Using the PRE



Moreover, very recently, the first purposely done experiments to use the PRE and alkoxyamines in radical chemistry have been presented by Studer and Ciufolini et al. (Scheme 2).[12] Consequently, knowledge of k_d is also useful for the synthetic planning of nitroxyl-mediated tin free radical chemistry.[13,14]

For selected cases, the enthalpic and steric factors that influence k_d have been addressed before.[15−23] Studies on 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)−alkoxyamines have recently shown a relationship between E_a or log k_d and bond dissociation energy (BDE(C−ON)[24,25] or BDE(C−H)[13,26]) of the leaving alkyl radical, suggesting that stabilization of the leaving alkyl radical is a major factor. Such a relationship also seemed valid for other alkoxyamines based on *N*-(2-

* To whom correspondence should be addressed: Fax 33-4-91-28-87-58; e-mail marque@srepir1.univ-mrs.fr.

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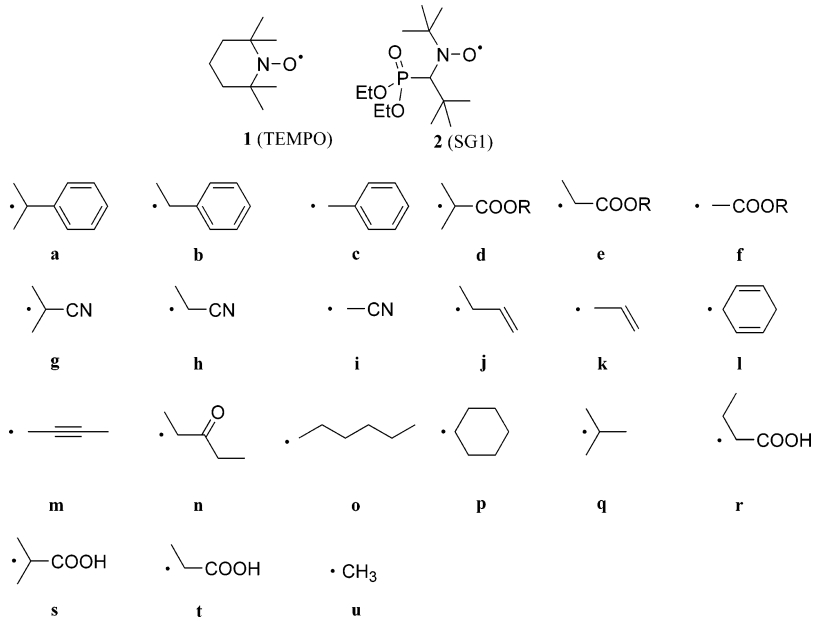
Scheme 3



methyl-2-propyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1) and di-*tert*-butylnitroxyl (DBNO) moieties.[26] However, it gives only a rough estimation of the value of k_d and is strongly dependent on the accuracy of the value of BDE(C−H). Indeed, other effects such as steric and polar effects in the ground state can bias the values of BDE (C−H).[27−33] Furthermore, we have recently shown that the correlation log k_d vs BDE(C−H) for SG1 derivatives is more complicated than expected from the well-known TEMPO derivative case.[34] To overcome these difficulties, we present hereafter an analysis following a multiparameter approach[35] where log k_d is parametrized with the molecular descriptors corresponding to the polar inductive/field[36−41] (σ_U), steric[42,43] (υ), and the stabilization[44] (σ_{RS}) effects of the leaving alkyl radicals in the TEMPO− and SG1−alkoxyamine series. Scheme 3 shows the nitroxyl and alkyl moieties of the alkoxyamines.

Unfortunately, not all derivatives were available for the two nitroxyl fragments **1** and **2** (see Table 1). Alkyl radicals **a**, **b**, **d**, **e**, **g**, **h**, **j**, **o, q, s**, and **t** should be reasonable models for the propagating radical of α-methylstyrene, styrene, methacrylates, acrylates, methacrylonitrile, acrylonitrile, butadiene, ethylene, isoprene, methacrylic acid, and acrylic acid, respectively.

Experimental Section

All reactions were carried out in oven-dried glassware under an argon atmosphere. Benzene (98%), copper bromide (98%), copper powder (99%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (99%), and 2-bromobutyric acid (97%) were used as received from Aldrich. The 2-bromo-2-methylpropionic acid (98%) was purchased from Fluka and used as received. TEMPO (98%, Lancaster) was sublimed, and SG1 (85% purity, Arkema group) was used as received. The solvent *tert*-butylbenzene (*t*-BuPh, Aldrich) was purified by standard procedures.[45] NMR experiments were performed in $CDCl_3$ as solvent on a 300 Avance Bruker spectrometer (^{1}H 300 MHz, ^{13}C 75.48 MHz, and ^{31}P 121.59 MHz) in "Centre Regional de RMN" in Marseille. Chemical shifts were given with TMS as internal reference for ^{1}H NMR, $CDCl_3$ (internal reference) for ^{13}C NMR, and H_3PO_4 85% (external reference) for ^{31}P NMR. Elemental analyses were done in "Service Commun de Micro Analyse Université d'Aix-Marseille 3". Alkoxyamines **2r** and **2s** were synthesized following a modified[21,23,25,34] Matyjaszewski procedure,[46] stored at −20 °C, and had a purity higher than 98%. Chromatography columns were performed using Merck silica gel 60.

General Procedure for the Synthesis of Alkoxyamines 2r and 2s. Under an inert atmosphere, a solution of SG1 (5 mmol, 1.47 g) and alkyl bromide (10 mmol, 1.67 g of 2-bromobutyric acid or 2-bromo-2-methylpropionic acid) in benzene (8 mL) was transferred to a mixture of CuBr (10 mmol, 1.43 g), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (20 mmol, 3.47 g), and Cu(0) (5 mmol, 0.64 g) in benzene (8 mL). After 3 h stirring at room temperature, 30 mL of water was poured into the mixture which was washed with diethyl ether (3 × 20 mL). The aqueous layer was saturated with NH_4Cl and then extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure afforded **2r** (1.34 g, 70%) as a mixture of two diastereoisomers and **2s** (1.43 g, 75%). The diastereoisomers of **2r** were further separated by silica gel column chromatography (ethyl acetate).

***N*-(2-Methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(1-carboxylpropyl)hydroxylamine (2r).** Anal. Calcd for $C_{17}H_{36}NO_6P$ (381.44): C 53.53; H 9.51; N 3.67. Found: C 53.54; H 9.66; N 3.91. Isomer A: ^{31}P NMR ($CDCl_3$): 27.0. ^{1}H NMR ($CDCl_3$): 0.88 (t, $^3J_{H-H}$ = 14.0 Hz, 3H, $CHCH_2CH_3$), 1.09 (s, 9H, $C(CH_3)$), 1.12 (s, 9H, $C(CH_3)$), 1.31 (t, $^3J_{H-H}$ = 12.0 Hz, 3H, OCH_2CH_3), 1.29 (t, $^3J_{H-H}$ = 12.0 Hz, 3H, OCH_2CH_3), 1.6−2.0 (m, 1H, $CHCH_2CH_3$), 2.23−2.36 (m, 1H, $CHCH_2CH_3$), 3.35 (d, $^2J_{H-P}$ = 21.0 Hz, 1H, CHP), 3.9−4.4 (m, 5H, CH_2CH_3 and $CHCH_2$). ^{13}C NMR ($CDCl_3$): 174.0 (COOH), 86.8 (*CH*−COOH), 70.8 (d, $^1J_{C-P}$ = 210 Hz, *C*−P), 62.9 (*C*−N), 60.69 (d, $^2J_{C-P}$ = 12.0 Hz, CH_2−O−P), 60.2 (d, $^2J_{C-P}$ = 10.6 Hz, CH_2−O−P), 35.65 (d, $^2J_{C-P}$ = 7.5 Hz, P−CH*C*Me$_3$), 30.0 (d, $^3J_{C-P}$ = 8.5 Hz, $CHC(CH_3)_3$), 27.8 ($C(CH_3)$), 16.42 (d, $^3J_{C-P}$ = 8.7 Hz, P−OCH_2CH_3), 16.21 (d, $^3J_{C-P}$ = 10.6 Hz, P−OCH_2CH_3), 9.3 (CH_2CH_3). Isomer B: ^{31}P NMR ($CDCl_3$): 24.3. ^{1}H NMR ($CDCl_3$): 0.95 (t, $^3J_{H-H}$ = 14.0 Hz, 3H, $CHCH_2CH_3$), 1.12 (s, 9H, $C(CH_3)$), 1.14 (s, 9H, $C(CH_3)$), 1.26 (t, $^3J_{H-H}$ = 13.0 Hz, 3H, OCH_2CH_3), 1.28 (t, $^3J_{H-H}$ = 13.0 Hz, 3H, OCH_2CH_3), 1.6−2.0 (m, 1H, $CHCH_2CH_3$), 2.23−2.36 (m, 1H, $CHCH_2CH_3$), 3.31 (d, $^2J_{H-P}$ = 21.0 Hz, 1H, CHP), 3.9−4.4 (m, 5H, CH_2CH_3 and $CHCH_2$). ^{13}C NMR ($CDCl_3$): 173.3 (*C*OOH), 87, 0 (*CH*−COOH), 68.1 (d, $^1J_{C-P}$ = 206 Hz, *C*−P), 62.8 (*C*−N), 62.52 (d, $^2J_{C-P}$ = 19.7 Hz, CH_2−O−P), 62.16 (d, $^2J_{C-P}$ = 9.3 Hz, CH_2−O−P), 35.65 (d, $^2J_{C-P}$ = 7.5 Hz, P−CH*C*Me$_3$), 30.4 (d, $^3J_{C-P}$ = 8.7 Hz, $CHC(CH_3)_3$), 27.8 ($C(CH_3)$), 16.42 (d, $^3J_{C-P}$ = 8.7 Hz, P−OCH_2CH_3), 16.21 (d, $^3J_{C-P}$ = 10.6 Hz, P−OCH_2CH_3), 9.7 (CH_2CH_3).

Table 1. Experimental Arrhenius Parameters (A and E_a), Rate Constants k_d at 120 °C, and Corrected Activation Energies E_a^{corr} for Alkoxyamines Based on the Nitroxyl Fragments 1 and 2 (Structures Shown in Scheme 3)

alkoxyamines	runs	T (°C)[a]	A[b] (10^{14} s^{-1})	E_a[c] (kJ mol^{-1})	$k_{d,393}$[d] (s^{-1})	E_a^{corr}[e] (kJ mol^{-1})	ref
1a	9	70−92	2.0	115.7	8.5×10^{-2}	116.2	26
1b	17	90−150	2.5	133.0	5.2×10^{-4}	132.9	26
1c	2	131−150	(2.4)	145.5	1.1×10^{-5}		26
1d	16[f]	65−121	1.8	119.8	2.2×10^{-2}	120.7	26
1e	11[f,g]	90−151	1.0	139.0	3.4×10^{-5}	141.8	26
1f	2[f]	151	(2.4)	161.5	8.1×10^{-8}		26
1g	15	51−103	6.8	118.4	0.13	114.9	26
1h	7	100−152	8.9	137.9	3.4×10^{-4}	134.3	13
1j	3	101−131	(2.4)	126.4	3.8×10^{-4}		26
1k	2	109−130	(2.4)	139.2	7.5×10^{-5}		26
1l				79.4	6.7×10^{3}		24
1p	1	150	(2.4)	165.0	2.8×10^{-8}		26, 24
1q	3	130−151	(2.4)	145.8	1.0×10^{-5}		13
1u	2	503−533		192.3	6.6×10^{-12}		24
2b	20[h]	60−137	1.9	124.5	5.5×10^{-3}	125.2	26
2c	3	110−131	(2.4)	134.4	3.3×10^{-4}		26
2e	12[i,j]	80−132	3.5	128.4	3.0×10^{-3}	127.2	26, 70, 71
	4[j,k]	90−129	(2.4)	130.8	1.0×10^{-3}		
2f	3	130−150	(2.4)	149.1	3.6×10^{-6}		25
2h	1[l]	100	(2.4)	121.9	1.5×10^{-2}		34, 70
	1[l]	100	(2.4)	125.2	5.5×10^{-3}		
	2[m]	110	(2.4)	127.4	2.8×10^{-3}		
2i	3	120−140	(2.4)	136.0	2.0×10^{-4}		34
2k	3	100−130	(2.4)	131.9	7.1×10^{-4}		34
2m	3	90−120	(2.4)	130.0	1.3×10^{-3}		34
2n	6[h]	100−137	(2.4)	126.4	3.8×10^{-3}		34
2o	1[n]	150	(2.4)	169.2	7.8×10^{-9}		25
2p	1[n]	150	(2.4)	162.3	6.4×10^{-8}		25
2q	3[n]	120−140	(2.4)	139.7	6.5×10^{-5}		25
2r	3[o]	112−124	(2.4)	128.5	2.0×10^{-3}		this work
2s	3	60−81	(2.4)	112.3	0.28		this work
2t	4	100−120	(2.4)	132.9[p]	5.3×10^{-4}		70
				130.7[q]	1.0×10^{-3}		

[a] $T \pm 1$ °C. [b] Statistical errors smaller than a factor 2. Value in brackets is the average of all experimentally accessible frequency factors. [c] Statistical errors between 2 and 3 kJ mol^{-1}. [d] Values calculated with parameters from columns 4 and 5. [e] Rescaled values of E_a using a mean frequency factor (see text) when it was necessary; i.e., A different from 2.4×10^{14} s^{-1}. [f] R = t-Bu. [g] Values may be biaised due to a side reaction; see ref 80. [h] Both diastereoisomers show same rate constant. [i] Isomers RS/SR, ^{31}P NMR (C_6D_6), $\delta = 22.3$ ppm. [j] R = Me. [k] Isomers RR/SS, ^{31}P NMR (C_6D_6), $\delta = 23.0$ ppm. [l] Both isomers were not purified separately. Rate constants were estimated from a plot of eq 1 showing two slopes. [m] Only one isomer could be measured. ^{31}P NMR (C_6D_6) $\delta = 21.8$ ppm. [n] As k_d is slow, same side reaction as in ref 80 could occur. [o] Only one diastereoisomer ($\delta = 24.3$ ppm) was available pure. [p] $\delta = 25.6$ ppm in C_6D_6/t-BuPh. [q] $\delta = 22.9$ ppm in C_6D_6/t-BuPh.

***N*-(2-Methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*O*-(2-carboxylprop-2-yl)hydroxylamine (2s).** Anal. Calcd for $C_{17}H_{36}NO_6P$ (381.44): C, 53.53; H, 9.51; N, 3.67; Found: C, 53.57; H, 9.28; N, 3.77. ^{31}P NMR ($CDCl_3$): 26.2. ^{1}H NMR ($CDCl_3$): 1.15 (s, 9H, C(CH_3)), 1.24 (s, 9H, C(CH_3)), 1.33 (t, $^3J_{H-H} = 6$ Hz, 3H, CH_2CH_3), 1.36 (t, $^3J_{H-H} = 6$ Hz, 3H, CH_2CH_3), 1.61 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 3.42 (d, $^2J_{H-P} = 27$ Hz, 1H, CHP), 3.9−4.4 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): 176.5 (COOH), 84.5 (C−COOH), 70.8 (d, $^1J_{C-P} = 136$ Hz, C−P), 63.0 (C−N), 62.06 (d, $^2J_{C-P} = 6.6$ Hz, CH_2−O−P), 59.94 (d, $^2J_{C-P} = 7.5$ Hz, CH_2−O−P), 35.74 (d, $^2J_{C-P} = 6.0$ Hz, CMe$_3$), 29.5 (d, $^3J_{C-P} = 6.0$ Hz, P−CHC(CH_3)$_3$), 27.4 (C(CH_3)$_3$), 27.9 (CCH_3), 24.1 (CCH_3), 16.15 (d, $^3J_{C-P} = 6.0$ Hz, P−OCH$_2CH_3$), 15.77 (d, $^3J_{C-P} = 7.5$ Hz, P−OCH$_2$(CH_3)).

ESR Kinetic Experiments. ESR kinetic experiments were performed on a CW-ESR spectrometer (Bruker EMX) in conditions previously described,[7,10,13,21,26] using air (oxygen) as an alkyl radical scavenger and samples freshly prepared from pure compounds.

Results

Measurements of the Rate Constant of the C−ON Bond Homolysis. Here, in the absence of monomers, we assumed that low molecular weight leaving alkyl radicals mimic polymerizing systems with similar substituted propagating alkyl radicals. Since there is no propagation in the present case and $n = 0$, only reactions 1, 2, and 4 (Scheme 1) should occur. Re-formation of the alkoxyamine by reaction 2 increases its apparent lifetime considerably. Therefore, k_d cannot be taken directly from its decay under normal reaction conditions.[4,7,8,26] Instead, conditions have to be chosen such that the transient radicals are rapidly and completely converted into other unreactive species (reaction 4) before reaction 2 (Scheme 1) can occur. In our earlier works,[7,26] we showed that k_d can be measured conveniently by quantitative CW-ESR spectroscopy from the appearance of the nitroxyl radical signal using a suitable alkyl radical scavenger such as galvinoxyl, TMIO-^{15}ND$_{12}$ (perdeuterated 2,2,10,10-tetramethylisoindolin-[^{15}N]-*N*-oxyl), TEMPO, and air (oxygen). Other authors have employed nitroxyl radicals,[18] styrene,[15−23,47] good hydrogen donors,[24,48] diiodine or nitroso compounds,[49] and oxygen.[20,49,50] The experimental cleavage rate constants k_d were measured using either the plateau method (eq 1) or the initial slope (eq 2) of the time evolution of the doubly integrated ESR signal of the growing nitroxyl radical in the presence of oxygen as alkyl radical scavenger.[7,10,13,21,25,26]

$$\ln\left(\frac{[\text{nitroxide}]_t - [\text{nitroxide}]_\infty}{[\text{nitroxide}]_\infty}\right) = -k_d t \qquad (1)$$

$$\frac{[\text{nitroxide}]_t}{[\text{nitroxide}]_\infty} = k_d t \qquad (2)$$

Table 2. Values of the Universal Electrical Hammett Constant σ_U, the Steric Constant v, the Corrected (RSE^{corr}) and Uncorrected (RSE) Radical Stabilization Energy, the Radical Stabilization Constants σ_{RS} and $\sigma^\bullet$, and Bond Dissociation Energy of the C−H Bond BDE(C−H) of the Alkyl Fragments a−u (Structures Shown in Scheme 3)

alkyl fragment	σ_U[a]	v[b]	RSE[c] (kJ mol^{-1})	RSE^{corr} [d] (kJ mol^{-1})	σ_{RS}[d]	$\sigma^\bullet$ [e]	BDE(C−H)[f] (kJ mol^{-1})
a	0.05	1.28[g,h]	−35.1	−53.1	0.36	2.46[i]	352.8 (6.3)[j]
b	0.07	0.86[g,k]	−35.1	−49.3	0.34	2.11[l]	357.0 (6.3)[j]
c	0.03	0.70	−35.1	−44.7	0.31	1.73	370.0 (6.3)[m]
d	0.07[n]	1.43[g,o,p]	−11.7	−29.7	0.20	1.16[q]	379.0 (15.0)[r]
e	0.09[s]	1.00[g,p,t]	−11.7	−25.9	0.18	0.81[u]	385.0 (15.0)[r]
f	0.15	0.80[g,p,v]	−11.7	−21.3	0.15	0.43[w]	406.3 (10.5)[r]
g	0.14[n]	1.20[g,x]	−14.2	−32.2	0.22	1.15[y]	362.6 (8.4)[z]
h	0.17[s]	0.79[g,aa]	−14.2	−28.4	0.19	1.10[bb]	375.8 (9.6)[z]
i	0.20	0.58[g,cc]	−14.2	−23.8	0.16	0.72	396.3 (8.8)[z]
j	0.03[s]	0.86[g,dd]	−52.7	−66.9	0.46	2.43[ee]	354.0 (6.3)[ff]
k	0.02	0.69	−52.7	−62.3	0.43	2.05	368.8 (8.8)[m]
l	0.07[s]	1.50[d,gg]	−62.6[hh]	−78.8	0.54	-[ii]	321.9 (6.3)[ij]
m	0.12[kk]	0.72	−27.9[ll]	−37.5	0.25	1.5[mm]	364.5 (8.4)[j]
n	0.09[s]	0.82[g,nn]	−26.8[oo]	−41.0	0.28	0.84[pp]	385.8 (5.9)[j]
o	−0.01[kk]	0.73	0.0	−9.6	0.07	0.42	422.6 (1.7)[qq]
p	0.00	0.87	0.0	−14.2	0.10	0.80	399.6 (4.0)[m]
q	−0.01	1.24	0.0	−18.0	0.12	1.15	404.0 (1.7)[m]
r	0.09[s]	1.02[g,rr]	−12.3[ss]	−26.5	0.18	0.78[tt]	394.5[tt]
s	0.07[n]	1.24[g,uu]	−12.3[ss]	−30.3	0.21	1.13[vv]	388.5 (12.1)[ww]
t	0.09[s]	0.83[g,xx]	−12.3[ss]	−26.5	0.18	0.78[yy]	394.5 (12.1)[zz]
u	−0.01	0.52	0.0	0.0	0.00	0.00	438.5 (0.4)[m]

[a] Values given in ref 58 unless otherwise mentioned. [b] Values given in refs 42 and 43 unless otherwise mentioned. [c] Values given in ref 55 unless otherwise mentioned. One assumed that primary alkyl radicals exhibit same RSE as secondary and tertiary. [d] See text. [e] Values given in ref 57 unless otherwise mentioned. [f] Errors are given in parentheses. [g] Estimated from eq 13. [h] $v_1 = v$(*t*-Bu) and $v_2 = v$(Ph) = 0.57. [i] Value of $\sigma^\bullet(PhCH_2)$ incremented of 0.73; see ref 57. [j] Reference 76. [k] $v_1 = v$(*i*-Pr) = 0.76 and $v_2 = v$(Ph) = 0.57. [l] Value of $\sigma^\bullet(PhCH_2)$ incremented of 0.38; see ref 57. [m] Reference 64. [n] Estimated from eq 12. [o] $v_1 = v$(*t*-Bu) and $v_2 = v(CO_2Alk) = 0.9$. [p] In the case of TEMPO derivatives, the type of R group (Me or *t*-Bu) does not modify the values of k_d unlike for SG1 derivatives; see refs 81 and 82. [q] Value of $\sigma^\bullet(MeOOCH_2)$ estimated in footnote *w* incremented of 0.73; see ref 57. [r] For **d** and **e** groups, see ref 77. For **f** group, see ref 83. [s] Estimated from eq 11. [t] $v_1 = v$(*i*-Pr) = 0.76 and $v_2 = v(CO_2Alk) = 0.9$. [u] Value of $\sigma^\bullet(MeOOCH_2)$ estimated in footnote *w* incremented of 0.38; see ref 57. [v] $v_1 = v$(Et) 0.52 and $v_2 = v(CO_2Alk) = 0.9$. [w] Value estimated using eq 32 and $a_{H,\beta}(MeOOCCMeH^\bullet)$ = 24.68 G from refs 55 and 84. [x] $v_1 = v$(*t*-Bu) and $v_2 = v$(CN) = 0.40. [y] Value of $\sigma^\bullet(NCCH_2)$ incremented of 0.73; see ref 57. [z] Reference 78. [aa] $v_1 = v$(*i*-Pr) = 0.76 and $v_2 = v$(CN) = 0.40. [bb] Value of $\sigma^\bullet(NCCH_2)$ incremented of 0.38; see ref 57. [cc] $v_1 = v$(Et) = 0.52 and $v_2 = v$(CN) = 0.40. [dd] $v_1 = v$(*i*-Pr) = 0.76 and $v_2 = v(CH{=}CH_2) = 0.57$. [ee] Value of $\sigma^\bullet(H_2C{=}CHCH_2)$ incremented of 0.38; see ref 57. [ff] Reference 26. [gg] A mean value between v(Ph) and $v(C_6H_{11})$ was assumed. [hh] Estimated from eq 3 in ref 55 and $a_{H,\alpha}$ = 13.56 G from ref 72. [ii] Cannot be estimated using eq 32. [jj] Reference 24. [kk] Estimated from eq 10. [ll] Estimated with eq 3 in ref 55 and $a_{H,\alpha}$ = 11.88 G of $MeC{\equiv}CCHMe^\bullet$ from ref 76. [mm] Value estimated using eq 32 and $a_{H,\beta}(MeC{\equiv}CCMeH^\bullet)$ = 19.16 G from ref 76. [nn] $v_1 = v$(*i*-Pr) = 0.76 and $v_2 = v$(Ac) = 0.50. [oo] Estimated with eq 3 and $a_{H,\alpha}$ = 19.7 G of $MeCOCH_2^\bullet$ from ref 55. [pp] Value of $\sigma^\bullet(H_3CCOCH_2) = 0.94$ incremented of 0.38; see ref 57. [qq] BDE(C−H) of C_2H_6 was used for C_6H_{14}; see ref 76. [rr] $v_1 = v$(*s*-Bu) = 1.02 and $v_2 = v(CO_2H)$ = 0.50. [ss] Estimated from eq 3 in ref 55 and $a_{H,\beta}$ = 21.6 G of $HOOCMe_2^\bullet$ and $a_{H,\alpha}$ = 20.1 from $HOOCHMe^\bullet$ from refs 74 and 75. Both values were averaged. [tt] One assumed that the presence of a methyl group in β position did not affect the values of $\sigma^\bullet$ and BDE(C−H) to a large extent. [uu] $v_1 = v$(*t*-Bu) and $v_2 = v(CO_2H) = 0.50$. [vv] Value of $\sigma^\bullet(HOOCCH_2)$ = 0.40 incremented of 0.73; see ref 57. [ww] $BDE(HOOCMe_2{-}H) = BDE(MeOOCMe_2{-}H) + 9.5$ kJ mol^{-1}. Increment given in ref 79. [xx] $v_1 = v$(*i*-Pr) = 0.76 and $v_2 = v(CO_2H)$ = 0.50. [yy] Value of $\sigma^\bullet(HOOCCH_2) = 0.40$ incremented of 0.38; see ref 57. [zz] $BDE(HOOCMeH{-}H) = BDE(MeOOCMeH{-}H) + 9.5$ kJ mol^{-1}. Increment given in ref 79.

The experiments were carried out in *t*-BuPh and SG1 used as the standard nitroxyl radical. We showed earlier that the frequency factor A for the C−ON bond homolysis for 30 alkoxyamines did not vary much with the alkoxyamine structure but lay between 10^{13} and 10^{15} s^{-1} with an averaged value A of 2.4×10^{14} s^{-1}.[7,13,21,25,26,34] For **2s** and **2r**, the rate constants were determined only at a few temperatures. Thus, the activation energies E_a were estimated directly from the rate constants k_d using the averaged frequency factor A. The estimated E_a values given in Table 1 correspond to the average of individual values over the temperature range. Individual values vary by less than 2 kJ mol^{-1} from the average values listed in Table 1. The number of experiments, temperature ranges, frequency factors A, activation energies E_a, cleavage rate constants at 120 °C $k_{d,393}$, and corrected activation energies E_a^{corr} for alkoxyamines based on the nitroxyl fragments **1** and **2** are listed in Table 1.

Bond Dissociation Energy BDE(C−H). We have recently shown[34] that the values of E_a for the homolysis of the CO−N bond of SG1−alkoxyamines were divided into two families (one nonpolar and one polar depending on the substituent carried by the leaving alkyl radical) when E_a was plotted against BDE(C−H) (eqs 3a and 3b).

$$E_a \text{ kJ mol}^{-1} = -133.0\ (250) \text{ kJ mol}^{-1} + 0.72\ (7) \times \text{BDE(C−H) kJ mol}^{-1} \quad R^2 = 0.97 \quad (3a)$$

$$E_a \text{ kJ mol}^{-1} = -137.0\ (780) \text{ kJ mol}^{-1} + 0.69\ (13) \times \text{BDE(C−H) kJ mol}^{-1} \quad R^2 = 0.77 \quad (3b)$$

The regression coefficient for the polar line is not good ($R^2 = 0.77$) due to a scattering of the data because the differences in E_a for the two isomers of **2e**, **2h**, and **2t** were not taken into account and due to the strongly deviating value of E_a of **2f**. Such deviation might be caused either by the large error on BDE(C−H) of $H{-}CH_2COOMe$ (see Table 2) or by a biased value of E_a due to side reactions. Alkoxyamine **2r** is not included in the regression because the statistic parameters are poorer ($R^2 = 0.61$). That is certainly due to some steric effect of the ethyl group of the **r** group. However, the value of E_a for **2r** lies close to the line corresponding to

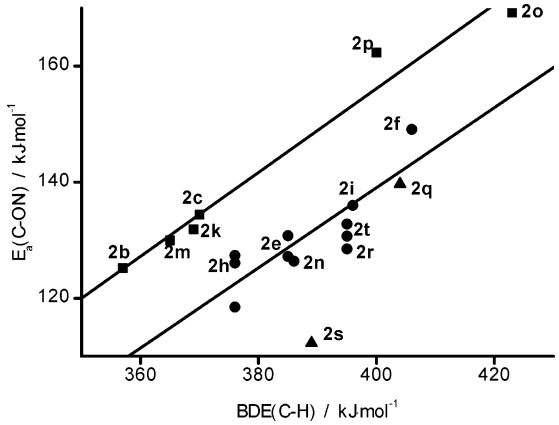


Figure 1. Activation energies E_a for the C−ON bond homolysis of alkoxyamines based on the nitroxyl fragment **2** vs bond dissociation energy BDE(C−H) of the corresponding hydrocarbon (structures shown in Scheme 3): (■) nonpolar (primary and secondary) leaving alkyl radicals; (●) polar (primary and secondary); and (▲) tertiary leaving alkyl radical (polar and nonpolar).

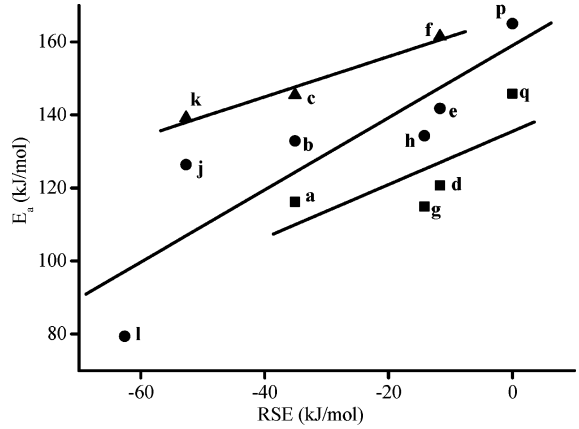


Figure 2. Activation energies E_a for C−ON bond homolysis in alkoxyamines based on the nitroxyl fragment **1** vs radical stabilization energy (RSE) of the leaving alkyl radicals: (■) tertiary, (●) secondary, and (▲) primary leaving alkyl radicals (structures shown in Scheme 3).

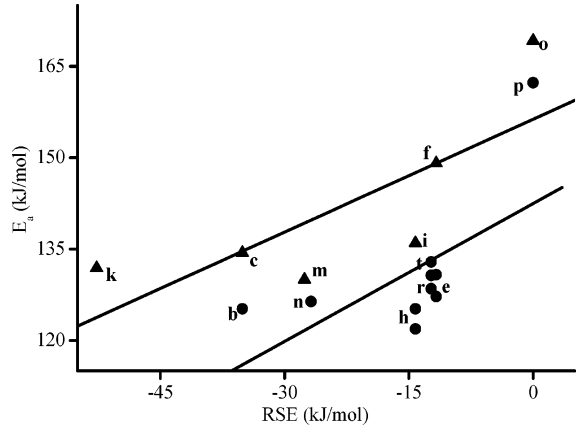


Figure 3. Activation energies E_a for C−ON bond homolysis in alkoxyamines based on the nitroxyl fragment **2** vs radical stabilization energy (RSE) of the leaving alkyl radicals: (●) secondary and (▲) primary leaving alkyl radicals (structures shown in Scheme 3).

the polar leaving alkyl radicals (Figure 1). In contrast, **2s** lies far from the two lines (polar and nonpolar radicals), which suggests a possible influence of the steric effect. Indeed, such a result could explain the position of **2q** on the line for polar leaving alkyl radicals (vide infra).

Radical Stabilization Energy. Some years ago, Rüchardt et al.[51−55] defined a radical stabilization energy (RSE), which was assumed free of any of the effects observed with BDE(C−H). Therefore, we plotted E_a vs RSE for TEMPO (Figure 2) and SG1 (Figure 3) derivatives. Assuming the same RSE for primary, secondary, and tertiary leaving alkyl radicals (Table 2), three lines (eqs 4−6) were drawn for TEMPO derivatives.

$$E_a^{corr}\ (\text{kJ mol}^{-1}) = 167.0\ (\pm 3.4) + 0.55\ (\pm 0.09) \times \text{RSE} \quad (4)$$
$$R^2 = 0.97,\ \sigma = 2.7,\ N = 3$$

$$E_a^{corr}\ (\text{kJ mol}^{-1}) = 159.0\ (\pm 10.3) + 0.99\ (\pm 0.28) \times \text{RSE} \quad (5)$$
$$R^2 = 0.76,\ \sigma = 15.4,\ N = 6$$

$$E_a^{corr}\ (\text{kJ mol}^{-1}) = 135.5\ (\pm 9.4) + 0.73\ (\pm 0.48) \times \text{RSE} \quad (6)$$
$$R^2 = 0.54,\ \sigma = 12.0,\ N = 4$$

The straight line for the primary (eq 4) alkyl radicals shows a high linear correlation coefficient ($R^2 = 0.97$), which suggests a major influence of RSE on k_d. The straight lines for the secondary (eq 5) and tertiary (eq 6) exhibit a poor R^2 (Figure 2). This scattering is certainly caused by some steric effect arising from the methyl group(s) on the carbon of the C−ON bond or by the peculiar conformation of the two six-membered rings (**p** and **l**) for the secondary alkyl radical.

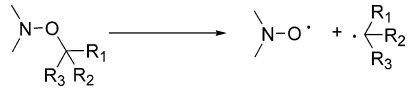
Although two straight lines (primary and secondary alkyl radicals) were drawn for SG1 derivatives, Figure 3 shows the scattered plots of E_a vs RSE which are underlined by small R^2 values (eq 7 for primary and eq 8 for secondary alkyl radicals). It is clear that the stabilization of the leaving alkyl radical is not the only factor to take into account. Further comments will be developed in the Discussion section.

$$E_a^{corr}\ (\text{kJ mol}^{-1}) = 156.3\ (\pm 7.3) + 0.62\ (\pm 0.25) \times \text{RSE} \quad (7)$$
$$R^2 = 0.60,\ s = 10.0,\ N = 6$$

$$E_a^{corr}\ (\text{kJ mol}^{-1}) = 142.5\ (\pm 5.8) + 0.75\ (\pm 0.33) \times \text{RSE} \quad (8)$$
$$R^2 = 0.39,\ s = 9.4,\ N = 10$$

Taft−Ingold Approach. To overcome the several difficulties[27] inherent in the use of BDE(C−H) as predictive tool and to gain more insight into the effects involved in the C−ON bond homolysis of the alkoxyamines, we investigated a multiparameter approach.[35] Indeed, one of us has already used this approach to disentangle the polar and steric effects of the nitroxyl moiety acting on the rate constant of the homolysis of the alkoxyamine C−ON bond.[56] From the previous approaches (vide supra) applied to the TEMPO and SG1 derivatives, it was obvious that the polar, steric, and radical stabilization effects of the leaving alkyl radicals influence k_d and are differently intertwined depending on the type of

Scheme 4



nitroxyl moiety. Thus, eq 9 should help to disentangle these effects by applying polar inductive/field (σ_U),[36−41] steric (υ),[42,43] and radical stabilization (σ_{RS} or $\sigma^\bullet$)[44,57] molecular descriptors to the leaving alkyl radicals.

$$\log k_d = \log k_{d,0} + \rho_{RS}\sigma_{RS} + \rho_U\sigma_U + \delta\upsilon \quad (9)$$

As the various substituents were directly bound to the reactive center (Scheme 4), the value of σ_U of the $CR_1R_2R_3$ group was used (Table 2).[58]

The unknown values were given by eqs 10−12 for primary, secondary, and tertiary alkyl groups, respectively.[59]

$$\sigma_{U,R_1CH_2} = 0.416\sigma_{U,R_1} - 0.0103 \quad (10)$$

$$\sigma_{U,R_1R_2CH} = 0.297\sum\sigma_{U,R} + 0.00482 \quad (11)$$

$$\sigma_{U,R_1R_2R_3C} = 0.248\sum\sigma_{U,R} + 0.00398 \quad (12)$$

For the steric demand, the constant of Charton[42,43] υ (Table 2) was preferred to the Taft[60] constants E_s because more groups were available, and the values were expected to be free of inductive and resonance effects.[42,43] The missing values were given by eq 13.[61]

$$\upsilon = 0.866\upsilon_1 + 0.436\upsilon_2 - 0.0455 \quad (13)$$

Values of υ_1 and υ_2 were given by Charton.[42,43,61] Furthermore, Charton showed that the υ_2 values for the ester group varies between 0.50 and 1.39 depending on the value of the dihedral angle θ between the COOR group and the reactive center.[61] Hence, for **1e** (R = Me) and for **2e** (R = Me), X-rays showed θ values of 60° and of 30°, respectively;[62] thus, a mean value of θ = 45 ° (i.e., υ_2 = 1.0) could be assumed for all derivatives in both series.[61] Intuitively, the **l** group (Scheme 3) looks more sterically demanding than the cyclohexyl (υ = 0.87)[42] but less than the phenyl group (υ = 2.15).[42] We thus chose a value υ = 1.5 to represent the size of the cyclohexadienyl group.[61]

The main problems arose with the radical stabilization molecular descriptor (σ_{RS}). In fact, the Hammett constants σ_U and σ_R (delocalization effect) are not the most suitable to take into account the radical stabilization.[28] A lot of work had already been done in that field but mainly on the benzylic-type compounds.[63] To the best of our knowledge, only Afanas'ev[57] developed in the 1970s a general scale for alkyl radical stabilization (vide infra). However, over the past two decades, Rüchardt's group[51−55] has developed a RSE scale for a large series of alkyl radicals. Those RSE values were assumed to be free of the ground-state effects involved in the homolysis of C−X bonds (X being any atom or group).[51−55] Moreover, the RSE values include the effects due to the electron-withdrawing, electron-donating, and resonance capacities of the various groups bound to the radical center. The RSE values are the same whatever the type of alkyl radicals studied and are given in kJ mol^{-1} (Table 2) and are not dimensionless like σ_U and υ.[55] The difference in the y-intercept of eqs 4−6 may be assumed as the stabilization due to the type (primary, secondary, and tertiary) of alkyl radical studied. However, these values are larger than those deduced from the BDE(C−H) of the corresponding alkane.[64] We supposed that some ground-state effects biased them. Consequently, we preferred to use the values given by Rüchardt et al.[53] and reported them in eqs 14−16 to give the corrected radical stabilization energy (RSE^{corr}, Table 2), RSE($CH_3^\bullet$) = 0.0 kJ mol^{-1} being the reference.

$$RSE^{corr}(\text{tertiary}) = RSE - 18.0 \text{ kJ mol}^{-1} \quad (14)$$

$$RSE^{corr}(\text{secondary}) = RSE - 14.2 \text{ kJ mol}^{-1} \quad (15)$$

$$RSE^{corr}(\text{primary}) = RSE - 9.6 \text{ kJ mol}^{-1} \quad (16)$$

To normalize the RSE^{corr} values, we used the formation enthalpy of the methyl radical ($\Delta H_f(CH_3^\bullet)$ = −146.3 kJ mol^{-1}) as it should contain a minimum of effects due to the saturated ground state of the molecule.[64] The values of σ_{RS} are given by eq 17.

$$\sigma_{RS} = \frac{RSE^{corr}}{\Delta H_f(CH_3^\bullet)} \quad (17)$$

The larger σ_{RS} is, the more stabilized the alkyl radical is. Before applying the σ_{RS} values to the multiparametric regressions, it had been checked that they were not correlated to σ_U (R^2 = 0.01) and υ (R^2 = 0.02).

A previous work[13] showed that a partial positive charge was present on the carbon of the polarized C−ON bond. Consequently, σ_R, σ_R^+, and σ_R^- (molecular descriptors for delocalization effect) were tested.[36,58] In the absence of one of the major parameters i.e., σ_U, σ_{RS}, and υ, R^2 and F-test values were very poor, and a four-parameter regression did not significantly improve the correlation. Therefore, for the moment, no experimental results justify the use of the resonance Hammett constants.

In earlier works,[13,26] plotting E_a(C−ON) vs BDE(C−H) showed that, for TEMPO derivatives, k_d was mainly influenced by the stabilization energy and also to a smaller extent by the size of the leaving alkyl radical. In contrast, plotting E_a(C−ON) vs BDE(C−H) for SG1 derivatives (Figure 1) emphasized the influence of the polarity of the leaving alkyl radical, besides the two precited effects.[34] Hence, all the possible correlation combinations with σ_{RS}, σ_U, and υ were tested and collected in Tables 3 and 4. For the TEMPO derivative series, eqs 18−20 suggest that radical stabilization is the major factor—but the statistical data (R^2 = 0.59) are worse than with BDE(C−H) as expected—and also that the effect of the size of the leaving alkyl radical is not negligible (R^2 = 0.49) whereas the polarity seems unimportant (R^2 = 0.10). The statistical data of eqs 18−20 are improved by eqs 21 and 23 (biparametric regressions). They could be further improved by removing deviating data such as those corresponding to the tertiary alkyl radicals or compounds **1b,c,j** and **k**. Equation 22 (Table 3) shows very good R^2 and F-test values, which confirms the influence of the size and stabilization of the leaving alkyl radical. Equation 24 (three parameters) improves the statistical data of eq 22. It will thus be considered as the equation giving the better description of the effects influencing C−ON bond homolysis in alkoxyamines (Figure 4, vide infra). The discrepancy observed with **1f** is certainly due to the

Table 3. Correlations of log k_d at 120 °C with Various Molecular Descriptors (Radical Stabilization Constant σ_{RS}, Universal Electrical Hammett Constant σ_U, and Steric Constant υ) for Alkoxyamines Based on the Nitroxyl Fragment 1

eq	log $k_{d,0}$	ρ_{RS}	ρ_U	δ	N^a	s^b	$R^{2\,c}$	t^d	F^e
18[f]	−8.4 (±1.3)	17.7 (±4.3)			14	2.4	0.59	99.87	
19	−5.0 (±1.4)		19.3 (±16.6)		14	3.5	0.10	77.00	
20	−11.3 (±2.2)			7.2 (±2.2)	13[g]	2.2	0.49	99.20	
21[h]	−9.5 (±1.3)	17.6 (±3.9)	18.4 (±10.3)	-	14	2.2	0.68	99.97[i] 91.80[j]	99.82[k]
22[l]	−14.3 (±1.1)	13.8 (±2.2)		7.0 (±1.1)	14	1.2	0.91	99.99[i] 99.99[m]	99.99[n]
23[o]	−13.2 (±2.3)	-	12.8 (±11.3)	8.7 (±2.2)	14	2.4	0.63	72.00[j] 99.77[m]	97.60[p]
24	−14.8 (±0.7)	13.9 (±0.9)	13.6 (±3.2)	6.6 (±0.7)	14	0.8	0.96	99.99[i] 99.45[j] 99.99[m]	99.99[q]

[a] Number of data. [b] Standard deviation. [c] Square of the coefficient of the linear regression. [d] Student *t*-test given in percent. [e] *F*-test given in percent. [f] Tertiary alkyl radicals were out of the general trend but included in the regression. [g] **1l** was not included because it was far from the straight line. [h] Tertiary alkyl radicals were slightly deviating from the regression line. [i] *t*-test on the value of ρ_{RS}. [j] *t*-test on the value of ρ_U. [k] *F*-test value is 12. [l] **1g,h** were slightly deviating. [m] *t*-test on the value of δ. [n] *F*-test value is 56. [o] **1b,c,j,k** were slightly deviating. [p] *F*-test value is 6. [q] *F*-test value is 80.

Table 4. Correlations of log k_d at 120 °C with Various Molecular Descriptors (Radical Stabilization Constant σ_{RS}, Universal Electrical Hammett Constant σ_U, and Steric Constant υ) for Alkoxyamines Based on the Nitroxyl Fragment 2

eq	log $k_{d,0}$	ρ_{RS}	ρ_U	δ	N^a	s^b	$R^{2\,c}$	t^d	F^e
25	−11.7 (±0.8)	49.6 (±4.6)			14[f]	0.7	0.89	99.99	
26	−3.6 (±0.2)		9.0 (±2.3)		14[g]	0.4	0.57	99.81	
27	−5.6 (±0.9)			3.6 (±1.0)	15[h]	0.6	0.49	99.66	
28[i]	−6.9 (±1.0)	11.1 (±3.9)	13.8 (±5.1)		19	1.4	0.49	99.00[j] 98.40[k]	99.52[l]
29	−9.4 (±2.2)	12.6 (±4.2)		4.1 (±2.2)	19	1.5	0.39	99.10[j] 92.40[m]	98.13[n]
30	−9.1 (±2.2)		17.7 (±5.9)	4.9 (±2.2)	19	1.5	0.39	99.13[k] 95.55[m]	98.17[o]
31	−14.3 (±1.3)	15.3 (±2.2)	19.5 (±3.0)	7.0 (±1.1)	19	0.8	0.85	99.99[j] 99.99[k] 99.99[m]	99.99[p]

[a] Number of data. [b] Standard deviation. [c] Square of the coefficient of the linear regression. [d] Student *t*-test given in percent. [e] *F*-test given in percent. [f] **2b,c,k,m**, and **n** were not included in the regression because they were far from the trend; $R^2 = 0.25$. [g] **2f,i,o,p,** and **s** were not included in the regression because they were far from the trend; $R^2 = 0.21$. [h] **2f,o,p**, and **q** were not included in the regression because they were far from the trend; $R^2 = 0.06$. [i] Tertiary alkyl radical were deviating from the regression line. [j] *t*-test on ρ_{RS}. [k] *t*-test on ρ_U. [l] *F*-test value is 8. [m] *t*-test on δ. [n] *F*-test value is 5. [o] *F*-test value is 5. [p] *F*-test value is 29.

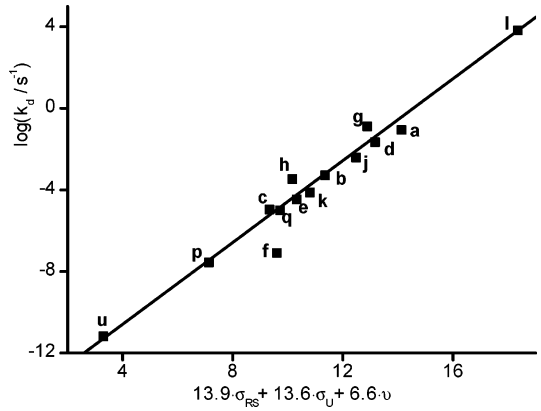


Figure 4. Log k_d at 120 °C for the C−ON bond homolysis in alkoxyamines based on the nitroxyl fragment **1** vs linear combination of molecular descriptor (radical stabilization constant σ_{RS}, universal electrical Hammett constant σ_U, and steric constant υ) for eq 24 (structures shown in Scheme 3).

position of the ester group; i.e., such a group can adopt any position, from the least to the most sterically demanding position.[60,61]

For the SG1 derivatives, the plot E_a(C−ON) vs BDE(C−H) (Figure 1) suggests clearly that the polar, radical stabilization and steric effects due to the leaving alkyl radical are strongly intertwined, each one acting significantly. As for TEMPO derivatives, all of the possible linear regression combinations with σ_{RS}, σ_U, and υ were tested and are collected in Table 4. As expected from Figure 1 and eqs 7 and 8, log k_d can be correlated to σ_{RS}, σ_U, and υ neither individually (eqs 25−27) nor dually (eqs 28−30), even by removing some deviating data whereas the R^2 value was lower than 0.2 when the 19 data were used. In contrast, the correlation with three parameters (eq 31 and Figure 5) exhibits significantly improved R^2 and *F*-test values. Equation 31 confirms the assumptions done from Figure 1 about the effects influencing the C−ON bond homolysis. Here also **2f** lies clearly far from the regression line. That behavior is certainly due to the reasons mentioned above for the TEMPO series. The scattering of the SG1 derivatives looks worse than that of TEMPO derivatives because the multiple parameter regression cannot account for the different k_d of the diastereoisomers.

Radical Hammett Constant $\sigma^\bullet$. As mentioned above, only Afanas'ev[57] has developed a general $\sigma^\bullet$ scale based either on kinetic measurements or on the hyperfine coupling constant of the β hydrogen of the alkyl radical MeXHC$^\bullet$ (eq 32).

$$\sigma^\bullet = 5.16 - 0.192a_{H\beta}(G) \qquad (32)$$

That $\sigma^\bullet$ scale is highly correlated to our σ_{RS} ($R^2 = 0.80$), and therefore the statistical data listed in Tables 5 and 6 and Tables 3 and 4 are similar. Nevertheless, the correlations are clearly better when σ_{RS} values are used instead $\sigma^\bullet$ values due to (i) σ_{RS} (see eqs 14−17) is more

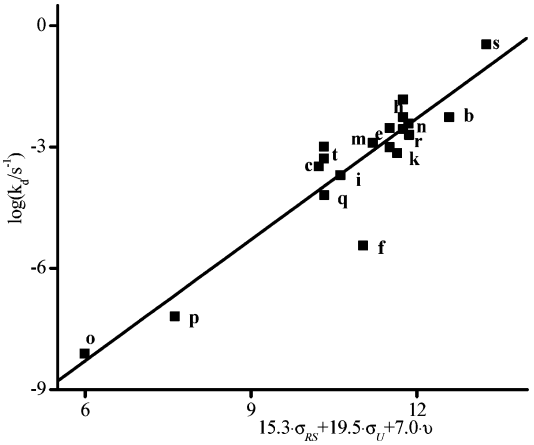


Figure 5. Log k_d at 120 °C for the C−ON bond homolysis in alkoxyamines based on the nitroxyl fragments **2** vs linear combination of molecular descriptor (radical stabilization constant σ_{RS}, universal electrical Hammett constant σ_U, and steric constant υ) for eq 31 (structures shown in Scheme 3).

general than $\sigma^\bullet$, i.e., almost any σ_{RS} of alkyl radical can be estimated; (ii) σ_{RS} values are based on RSE values and only correlated to hyperfine coupling constants of α or β hydrogen of alkyl-centered radical;[55] (iii) such values should be mainly free of ground-state effects;[51−55] (iv) some discrepancies (see Table 2) were observed between the values of σ_{RS} and $\sigma^\bullet$, e.g., $\sigma^\bullet(CMe_2CN) < \sigma^\bullet(t\text{-Bu})$ ....

Discussion

We[34] showed that, for the SG1−alkoxyamines (Figure 1 and eqs 3a,b), the leaving alkyl radical carrying a polar group bound to the radical center cleaves faster contrary to the TEMPO derivatives for which no influence of the polarity was observed, e.g., k_d(**2h**) ≈ k_d(**2b**). As expected, the values of E_a for **2t** (**t** being a polar group) lie close to the straight line corresponding to polar leaving alkyl radicals. The large gap between E_a for **2s** and the straight line ascribed to the polar leaving alkyl radicals confirms our previous assumption[34] about the behavior of **2q**. That is, besides a polar effect acting on k_d, there is also a steric effect involved. In Figure 1, the gaps between E_a of **2q** and E_a of **2s** and the lines representing eqs 7 and 8−18 and 20 kJ/mol, respectively—are quite similar, which suggests that the steric effect acts similarly in both series. Then, when a "*polar*" nitroxyl radical is used, one needs to draw four different correlations (polar and nonpolar primary plus secondary, and the same for tertiary alkyl fragments) to take into account the major effects involved in the C−ON bond homolysis. Consequently, plotting E_a vs BDE(C−H) is not the best tool to predict values of k_d easily and accurately or to determine and analyze the effects influencing the C−ON bond cleavage. In fact, BDE(C−H) is composed of various effects involved in the stability of the molecule in the ground state.[27−33]

For a better insight into the factors influencing the C−ON bond homolysis, we plotted E_a vs RSE (radical stabilization energy)[51−55] for TEMPO (Figure 2) and SG1 (Figure 3) derivatives. For TEMPO−alkoxyamines, the three straight lines in Figure 2 show that the radical stabilization is the major effect involved in the C−ON cleavage. The scattered plot for the secondary and tertiary alkyl radicals suggests that the size of the leaving alkyl radical has an influence. In contrast, with SG1 derivatives, although two parallel lines for primary and secondary alkyl radicals were drawn (Figure 3, but with poor statistical tests), the scattered plots exemplify unambiguously that the radical stabilization does not have a major influence on the C−ON bond cleavage, as expected from Figure 1. Indeed, for both series, a multiple parameter approach[35] (eqs 21−24 and 28−31) turned out to be very powerful because the values of k_d were correlated with three parameters: σ_U (Hammett constants for the universal electrical effect, i.e., localized electrical or polar inductive/field effect),[36−41,58,59] σ_{RS} (Hammett constants for the radical stabilization effect), and υ (constants for the steric effect).[42,43,61] For the TEMPO−alkoxyamine series, good correlations were obtained with one (σ_{RS}, eq 18) or two (σ_{RS} and υ, eq 22) parameters, but the three-parameter linear regression (eq 24) gave even better results that can be compared to the results obtained with the SG1−alkoxyamine series.

Using eqs 41 and 42,[65] with X_i the value of the parameter X for the ith data, $\bar{X}$ the arithmetic mean of the X parameter, n the number of data, ν the number of degree of freedom, α_X the weighting coefficient, and C_X the coefficient of the X parameter, it was possible to estimate the weight of the various effects in each series.

$$\alpha_X = \sqrt{\frac{\sum_{i=1}^{n}(X_i - \bar{X})^2}{\nu}} \tag{41}$$

$$\%\, X = 100 \times \frac{\alpha_X C_X}{\sum_i \alpha_{X_i} C_{X_i}} \tag{42}$$

Entry 1 (Table 7) reveals that, in TEMPO series, radical stabilization (44%) and steric (40%) demands are the main effects involved in the C−ON bond homolysis. Indeed, the polar field/inductive effect (16%) is weak but not negligible. Those results are in good agreement with what was observed in Figure 2 and earlier works.[13,25,26] In contrast, in SG1 series (entry 2, Table 7), the absence of major effects of the leaving alkyl radicals—radical stabilization effect: 34%; steric effect: 31%; and the polar (universal electrical) effect: 35%—confirms the remarks made about Figure 3 (no main influence of radical stabilization) and about Figure 1 (four correlations to explain the results). Although SG1 is bulkier than TEMPO, its size has a smaller influence than TEMPO's (35% for TEMPO against 31% for SG1). Moreover, the radical stabilization effect is lower in the SG1−alkoxyamine series (34%) than in the TEMPO−alkoxyamine series (44%). Conversely, the influence of the electrical effect (σ_U) is 2 times higher in the SG1−alkoxyamine series (35%) than in TEMPO−alkoxyamine series (16%), which suggests that the leaving alkyl radical is highly sensitive to the polarity of the nitroxyl moiety.

All of these results are accounted for by changes in the transition state (TS), ground state (GS), and final state (FS) and are sketched in Figure 6 for nonpolar leaving alkyl radicals. For both the nitroxyl and alkyl moieties, an increase of k_d with the increasing steric demand is a feature of a destabilization in GS. Otherwise, in the TS increasing steric demand involves a smaller $\Delta S^\ddagger$; thus, a larger $\Delta G^\ddagger$ and consequently k_d is smaller. With respect to the Hammond principle,[66] one

Table 5. Correlations of log k_d at 120 °C with Various Molecular Descriptors (Radical Stabilization Constant $\sigma^\bullet$, Universal Electrical Hammett Constant σ_U, and Steric Constant v) for Alkoxyamines Based on the Nitroxyl Fragment 1

eq	log $k_{d,0}$	$\rho^\bullet$	ρ_U	δ	N^a	s^b	$R^{2\,c}$	t^d	F^e
33	−7.9 (±1.2)	2.7 (±0.8)			13	2.2	0.49	99.30	
34	−9.7 (±1.1)	2.9 (±0.6)	23.0 (±8.0)		13	1.7	0.72	99.90[f] 98.32[g]	99.84[h]
35	−13.1 (±1.6)	2.3 (±0.6)		6.0 (±1.6)	13	1.5	0.79	99.77[f] 99.63[i]	99.86[j]
36	−13.8 (±0.9)	2.5 (±0.3)	18.9 (±4.0)	5.2 (±0.9)	13	0.8	0.94	99.99[f] 99.89[g] 99.97[i]	99.99[k]

[a] Number of data. [b] Standard deviation. [c] Square of the coefficient of the linear regression. [d] Student t-test given in percent. [e] F-test given in percent. [f] t-test on $\rho^\bullet$. [g] t-test on ρ_U. [h] F-test value is 13. [j] F-test value is 19. [i] t-test on δ. [k] F-test value is 47.

Table 6. Correlations of log k_d at 120 °C with Various Molecular Descriptors (Radical Stabilization Constant $\sigma^\bullet$, Universal Electrical Hammett Constant σ_U, and Steric Constant v) for Alkoxyamines Based on the Nitroxyl Fragment 2

eq	log $k_{d,0}$	$\rho^\bullet$	ρ_U	δ	N^a	s^b	$R^{2\,c}$	t^d	F^e
37	−5.0. (±1.0)	1.5 (±0.8)			19	1.7	0.17	91.70	
38	−6.9 (±1.0)	2.0 (±0.7)	16.0 (±5.3)		19	1.4	0.47	98.67[f] 99.20[g]	99.37[h]
39	−7.5 (±2.3)	1.6 (±0.8)		2.9 (±2.3)	19	1.7	0.24	93.27[f] 76.40[i]	88.67[j]
40	−12.7 (±1.7)	2.3 (±0.5)	21.9 (±4.2)	5.9 (±1.6)	19	1.0	0.73	99.34[f] 99.99[g] 99.82[h]	99.84[k]

[a] Number of data. [b] Standard deviation. [c] Square of the coefficient of the linear regression. [d] Student t-test given in percent. [e] F-test given in percent. [f] t-test on $\rho^\bullet$. [g] t-test on ρ_U. [h] F-test value is 7. [i] t-test on δ. [j] F-test value is 3. [k] F-test value is 13.

Table 7. Weighting Coefficients for Eqs 24 and 31

entry	$\%\sigma_{RS}$	$\%\sigma_U$	$\%v$
1	44	16	40
2	34	35	31

can assume a late transition state, i.e., resembling FS. Therefore, any stabilization of both nitroxyl and alkyl radicals (FS) stabilizes TS and thus decreases E_a (increasing k_d). Oddly, an increase of k_d with the increasing polar effect was not expected because the electron-withdrawing groups destabilize both the nitroxyl and alkyl moieties in TS. Indeed, one of us has recently showed that electron-withdrawing groups on the nitroxyl radical destabilize FS (the form B is not stabilized by electron-withdrawing groups, Scheme 5) and therefore TS; i.e., the more electron−withdrawing the groups are, the smaller the values of k_d are.[13,56] Moreover, previous works suggest the presence of a partial positive charge on the carbon of the C−ON bond in TS.[13] One expects, a priori, a destabilization of TS with the increasing polarity of the alkyl moiety. Against these expectations, k_d is enhanced by electron-withdrawing groups on both moieties.

All of these effects caused by the polarity of both the nitroxyl and alkyl moieties are due to the polar ground-state effect (PGSE) described by Nau.[67] Moreover, in a previous work, one of the authors has already pointed out the influence of PGSE on the C−ON bond homolysis in para-substituted **1b** derivatives.[13] Such effect is very well-known for aromatic compounds,[33] recently[29−33] extended to any molecules, and it should account for our observations. Briefly, Pauling[68] has shown that BDE includes a polar term (ionic resonance energy E_i) which depends on the difference of electronegativity χ for the atoms or groups of the cleaved bond. From these grounds, Nau[67] has shown that BDE of the XR−Z molecule is described by eq 43.

$$\mathrm{BDE(XR{-}Z)} = {}^1/_2\mathrm{BDE(XR{-}RX)} + {}^1/_2\mathrm{BDE(Z{-}Z)} + 23(\chi_{XR} - \chi_Z)^2 + \sum E_{relax} \quad (43)$$

ΣE_{relax} covers the contribution of E_i for all bonds in XRZ except for the cleaved XR−Z bond, and it increments the value of E_i positively or negatively. Thus, Nau[67] has established that the PGSE between a molecule reference HR−Z and a homologue XR−Z is roughly described by eq 44.

$$\mathrm{PGSE} \equiv 23[(\chi_{HR} - \chi_Z)^2 - (\chi_{XR} - \chi_Z)^2] - \Delta\Sigma E_{relax} \quad (44)$$

A consequence of that approach is that the more mismatched the χ values are, the stronger the bond is. Assuming that eq 44 is also true when Z is a group of atoms and HR or XR is not merely a benzylic-type group, and setting, thus, O−TEMP (**1**) or O−SG (**2**) for Z and HR for nonpolar groups (NPG) and XR for polar groups (PG), eqs 45a and 45c describe the PGSE for the TEMPO and SG1 families, respectively.

$$\mathrm{PGSE}^{\mathbf{1}} = 23[(\chi_{NPG} - \chi_{OTEMP})^2 - (\chi_{PG} - \chi_{OTEMP})^2] - \Delta\Sigma E_{relax}{}^{\mathbf{1}} \quad (45a)$$

$$\Delta\Sigma E_{relax}{}^{\mathbf{1}} = 23(\chi_{PG} - \chi_{NPG})(\chi_{NPG} - \chi_{PG} - 2\chi_{TEMP}) \quad (45b)$$

$$\mathrm{PGSE}^{\mathbf{2}} = 23[(\chi_{NPG} - \chi_{OSG})^2 - (\chi_{PG} - \chi_{OSG})^2] - \Delta\Sigma E_{relax}{}^{\mathbf{2}} \quad (45c)$$

$$\Delta\Sigma E_{relax}{}^{\mathbf{2}} = 23(\chi_{PG} - \chi_{NPG})(\chi_{NPG} - \chi_{PG} - 2\chi_{SG}) \quad (45d)$$

When eqs 45a and 45c are combined to give eq 46a, it is obvious that the larger the difference of χ between **1** and **2** is, the stronger the ΔPGSE is and the more sensitive to the polar effect the C−ON bond is.

$$\Delta\mathrm{PGSE} = 46(\chi_{OSG} - \chi_{OTEMP})(\chi_{NPG} - \chi_{PG}) - \Delta\Delta\Sigma E_{relax} \quad (46a)$$

$$\Delta\Delta\Sigma E_{relax} = 46(\chi_{PG} - \chi_{NPG})(\chi_{SG} - \chi_{TEMP}) \quad (46b)$$

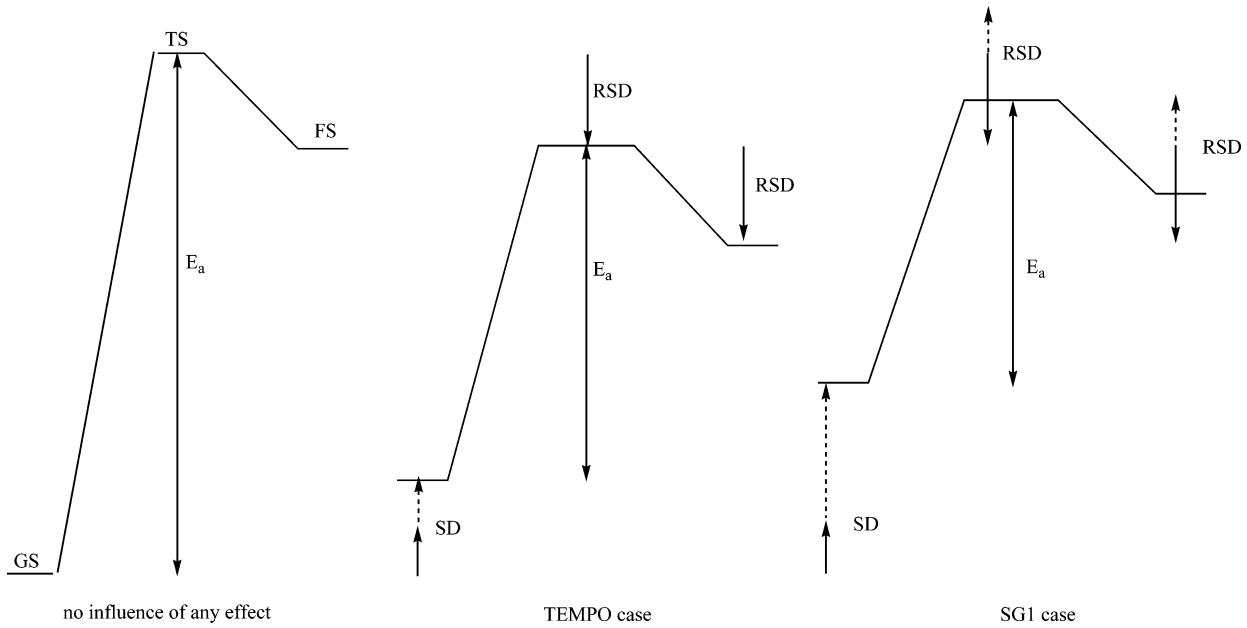
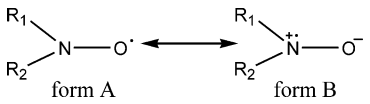


Figure 6. Influence of the steric (SD) and radical stabilization (RSD) demand on the ground state (GS), transition state (TS), and final state (FS) of alkoxyamines based on the nitroxyl fragments **1** and **2** and carrying nonpolar alkyl moieties. Bold and dotted arrows are for alkyl and nitroxyl moieties, respectively.

Scheme 5



The EPR nitrogen hyperfine coupling constants and the multiparametric approach of the effect of the nitroxyl moiety on the value of k_d support the view of radical **2** being more polar than radical **1**. Then, it is not surprising to observe a stronger PGSE in the SG1−alkoxyamine series than in the TEMPO−alkoxyamine series. It is worthwhile to point out that the difference in energy between polar and nonpolar groups due to the PGSE is roughly of 15 kJ/mol, which is probably the highest value observed for such effect. In general, for bond homolysis such a value is assumed around 5−10 kJ/mol.[67,69] The PGSE for the alkoxyamine **2** family is depicted in Scheme 6.[67] One can assume a polar $C^{\delta+}-^{\delta-}ON$ bond, and thus any electron-withdrawing group (EWG) destabilizes the ground state (Scheme 6a), and reversely for electron-donating groups (EDG) (Scheme 6b).

Hence, to predict a value of k_d from the structure of the alkoxyamine, the nitroxyl moiety has to be divided in two families, one polar and one nonpolar. In a recent work,[56] it has been shown that the polarity of the nitroxyl moiety is estimated with eq 47.

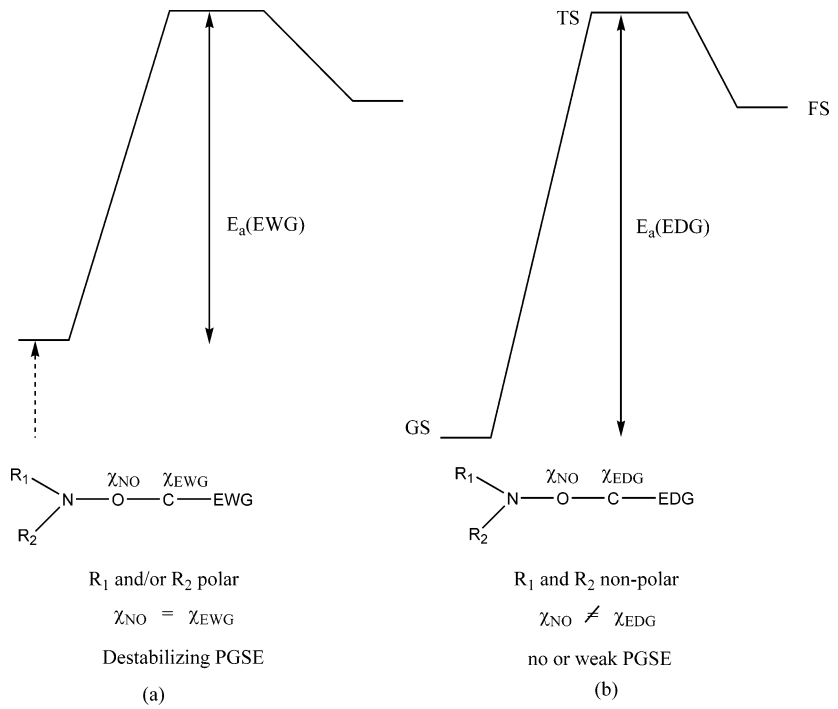
$$\sigma_U = \sum_{i=1}^{6} \sigma_{U,i} \qquad (47)$$

The difference (≈9.0 kJ mol^{-1}) of E_a between **3e** and **3b** is close to the difference observed between **1e** and **1b** (8.9 kJ mol^{-1}) rather than the one between **2e** and **2b** (4.0−6.3 kJ mol^{-1}), which implies **3** (Scheme 7) belongs to the nonpolar nitroxyl family (see footnotes of Table 8). On the other hand, the difference[25] (6.5 kJ mol^{-1}) of E_a between **5e** and **5b** is close to the difference observed between **2e** and **2b** (4.0−6.3 kJ mol^{-1}) rather than the one between **1e** and **1b** (≈9.0 kJ mol^{-1}), which implies **5** (Scheme 7) belongs to the polar nitroxyl fragment family (see footnotes of Table 8). Therefore, in first approximation, the nitroxyl moieties belonging to the nonpolar family should exhibit σ_U values (polar effect) smaller than 0.10, and those belonging to the polar family σ_U values larger than 0.10. Assuming that the coefficients (ρ_U, ρ_{RS}, and δ) determined for the nonpolar or polar nitroxyl fragment family can be applied respectively to any nitroxyl fragments belonging to one of the two families, thus the difference in influence of the nonpolar or polar nitroxyl fragment is contained in the constant term log $k_{d,0}$, i.e., the y-intercept which accounts for all effects due to the substituents of the nitroxyl fragment. Hence, the constant terms log $k_{d,0}$ for a few current nitroxyl fragments are given in Table 8 considering they belong either to the nonpolar or to the polar nitroxyl fragment family. Because of their σ_U values, the nitroxyl radicals **1**, **3**, and **4** belong to the nonpolar nitroxyl fragment family, but estimates of their constant terms log $k_{d,0}$ (values in italics) are also given in Table 8 considering the coefficients (ρ_U, ρ_{RS}, and δ) for the polar nitroxyl fragment. Similarly, because of their σ_U values, nitroxyl radicals **2**, **5**, and **6** belong to the polar nitroxyl fragment family, but estimates of their constant terms log $k_{d,0}$ (values in italics) are also given in Table 8 considering the coefficients (ρ_U, ρ_{RS}, and δ) for the nonpolar nitroxyl fragment family. Then, it is possible to estimate k_d values for alkoxyamines containing various nitroxyl fragments.

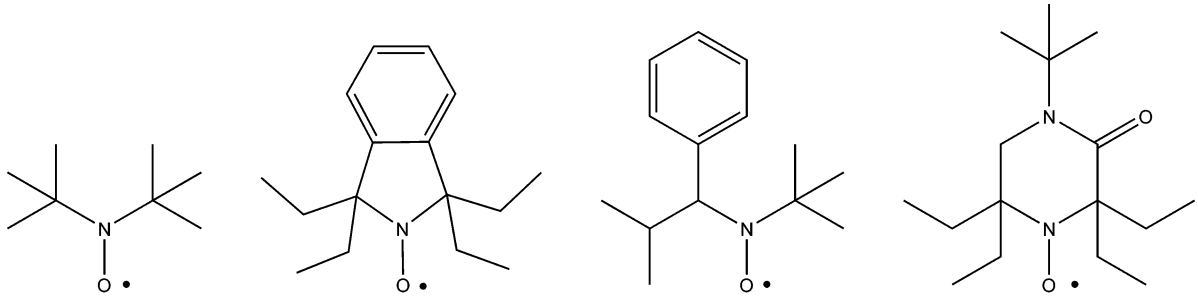
Conclusion

We have shown that the multiparameter approach provides a better and deeper insight into the effects (polar, steric, and radical stabilization demands) ruling the C−ON bond homolysis in alkoxyamines than any other approaches (BDE(C−H), RSE, or monoparametric correlations). Hence, we were able to disentangle the various intertwined effects (polar, steric, and radical stabilization effects), and we pointed out that the presence and the strength of each effect is dependent on the structure of the nitroxyl radical counterpart. It was shown that the polar effect depends strongly on the structure of the nitroxyl fragment; that is, for the

Scheme 6



Scheme 7



3 DBNO **4** **5** TIPNO **6**

Table 8. Values of log $k_{d,0}$ for Some Useful Nitroxyl Fragments[a]

	1	3[b]	4[c]	5[d]	6[e]	2
σ_U[f]	−0,06	−0.06	0.08	0.10	0.33	0.28
log $k_{d,0}$						
nonpolar	−14.9[g]	−13.2[g]	−14.0	*−13.8*[g]	*−13.5*	*−13.3*[g]
polar	*−16.0*[g]	*−14.5*[g]	*−15.2*	−15.0[g]	−14.7	−14.4[g]

[a] Estimated from eq 24 (nonpolar family) and eq 31 (polar family). Values in italics are for the estimation in the opposite family; see text. [b] DBNO is di-*tert*-butyl-*N*-oxyl radical. **3b**: $A = 2.2 \times 10^{14}$ s^{-1}, $E_a = 121.8$ kJ mol^{-1}. **3e**: $A = 1.2 \times 10^{14}$ s^{-1}, $E_a = 128.2$ kJ mol^{-1}. See ref 26. With $A = 2.4 \times 10^{14}$ s^{-1}, E_a(**3b**) = 122.1 kJ mol^{-1} and E_a(**3e**) = 130.4 kJ mol^{-1}. [c] **4b**: $A = 2.4 \times 10^{14}$ s^{-1}, $E_a = 128.0$ kJ mol^{-1}. See ref 56. [d] TIPNO is 2,2,5,5-tetramethyl-4-phenyl-3-azahexane-3-oxyl radical. **5b**: $A = 5.6 \times 10^{14}$ s^{-1}, $E_a = 129.6$ kJ mol^{-1}, see ref 26. **5e**: $A = 2.4 \times 10^{14}$ s^{-1}, $E_a = 133.4$ kJ mol^{-1}, see ref 25. With $A = 2.4 \times 10^{14}$ s^{-1}, E_a(**5b**) = 126.9 kJ mol^{-1}. [e] **6b**: $A = 2.4 \times 10^{14}$ s^{-1}, $E_a = 124.2$ kJ mol^{-1}. See ref 56. [f] Estimated with eq 47. [g] Averaged value of the **b** and **e** derivatives.

weakly polar nitroxyl fragment, the influence of the polarity of the leaving alkyl group on the homolysis is weak, whereas for the polar nitroxyl fragment, the influence of the polarity of the leaving alkyl group on the homolysis is strong. Moreover, combining eqs 24 and 31 and eq 8 ($\log(k_d/s^{-1}) = 3.07\sigma_I - 0.88E_s - 5.88$) of Marque[56] gives a powerful tool to predict accurate rate constants k_d with only a short glance to the structure of the alkoxyamine considered. Such system of equations should quickly turn out to be indispensable to design new alkoxyamines and to tune NMP experiments.

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