Re-formation Reaction of Cyclic Nitroxide-Based Alkoxyamines: Steric and Polar/Stabilization Effects

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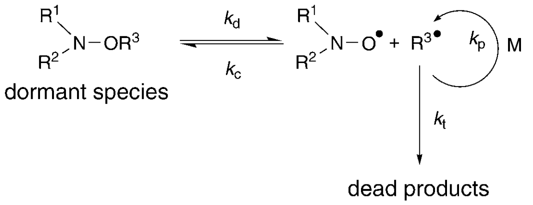
Dedicated to Professor *Hanns Fischer* for his invaluable contribution in the fields of nitroxide-mediated polymerization and radical chemistry

In nitroxide-mediated radical polymerization, the polymerization times decrease with the increasing re-formation rate constant of the C−ON bond (→ alkoxyamine) between the growing polymer chain and the nitroxide radical. The factors influencing the re-formation rate constant are of considerable interest, but up to now, the polar/stabilization effects have not been addressed thoroughly. The combination of new data with previously reported data now showed that the re-formation rate constant k_c increases with the increasing polar character of the substituents attached to the nitroxide moiety. The polar/stabilization effects are weaker for the re-formation than for the homolysis of the C−ON bond, and may be mainly attributed to the relocation of the odd electron onto the O-atom of the N−O moiety, *i.e.*, the stabilization of the nitroxide moiety. Hence, it is possible to predict the values of k_c by combining both the polar/stabilization (σ_I) and steric effects (E_s^1), *i.e.*, $\log(k_c/\text{M}^{-1}\ \text{s}^{-1}) = 9.86 + 0.57 \cdot \sigma_I + 0.40 \cdot E_s$.

Introduction. – Since the seminal work of *Rizzardo* [1][2] and *Georges* [3], nitroxide-mediated radical polymerization (NMP) has often been used for the synthesis of living polymers and copolymers with narrow polydispersities and controlled molecular masses and architecture [4–6]. The mechanism of NMP outlined in *Scheme 1* involves the cleavage of capped chain molecules (dormant species) into propagating alkyl and persistent nitroxide radicals (k_d). The propagating radicals grow by monomer addition (k_p) and form longer dormant chains by cross-coupling with the nitroxide radicals (k_c). Simultaneously, the usual self-termination (k_t) of the propagating radicals into unreactive polymer products takes place. This removes the propagating radicals and increases the concentration of nitroxide radicals over time; the cross-coupling reaction (k_c), therefore, dominates over self-termination [7][8]. For an extended time range, a quasi-equilibrium of the reversible cleavage exists which is characterized by weakly time-dependent radical concentrations and a large excess of the persistent radicals over the propagating radicals.

For the well-controlled and living radical polymerization of a given monomer with propagation and termination rate constants k_p and k_t, the rate constants of the reversible cleavage k_d and k_c must fall into proper ranges [7–9]. In general, one aims at rela-

Scheme 1. *Simplified Scheme of Nitroxide-Mediated Polymerization* (NMP). M = monomer.



tively large equilibrium constants $K = k_d/k_c$ because they yield large propagating-radical concentrations, and, hence, comparatively fast monomer conversion [7–9]. Furthermore, at a given time, the polydispersity index is smaller for larger k_d and k_c. Consequently, the determination of K and k_d has recently attracted considerable attention for both polymeric [10][11] and low-molecular-mass systems [12–17].

Up to now, most of the studies in this domain were devoted to the measurements of k_d and to the analysis of the effects of the subtituents attached to the nitroxide moiety on the strength of the C–ON bond [18]. However, it has appeared in the literature that values of k_c may play an important role in the fate of the polymerization [19][20]. *Siegenthaler* and *Studer* [20] have shown that the polymerization was *ca.* five times as fast with **B** than with **A** (*Fig. 1*) whereas $k_{d,\mathbf{A}} = k_{d,\mathbf{B}}$ but $k_{c,\mathbf{A}} > 40 \cdot k_{c,\mathbf{B}}$. Therefore, it is timely to analyze thoroughly the effects involved in the re-formation of alkoxyamines. This has been partially addressed by *Ingold* and co-workers [21][22] for a few nitroxide radicals with a large set of alkyl radicals and solvents, but very few radicals were of interest for the polymerization. *Fischer* and co-workers [23][24] measured k_c for both nitroxide and alkyl radicals used in NMP and revealed very weak temperature dependences; they showed with a small series of nitroxide radicals that k_c decreased with increasing congestion around the nitroxide moiety. In contrast to the many data gathered concerning the C–ON bond homolysis [16][17] – polar, stabilization, and steric effects for nitroxide and alkyl fragments, long-range steric and polar effects, intramolecular H-bonding, anomeric and anchimeric effects – and to the predictive relationships developed for k_d, not so many data have been collected concerning the re-formation reaction, and no predictive models have been developed for k_c. Therefore, using the new k_c measured in this work for nitroxide radicals **11**, **12**, **14**, and **15**, and those given in the literature [22–25] for nitroxide radicals **1**–**10**, **13**, and **16** (*Table 1*), we propose to rationalize the polar and steric effects of the substituents attached to the nitroxide moieties for the scavenging of the 1-phenylethyl radical in terms of a bi-parameter relationship (electrical *Hammett* constant σ_I for the polar effect, and modified *Taft* steric constant E_s for the steric effect).

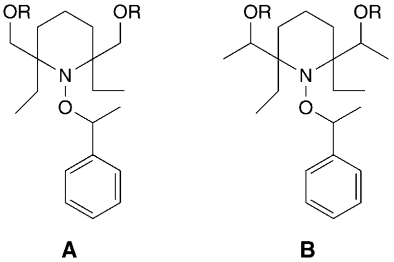


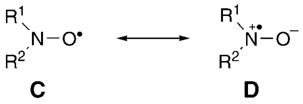
Fig. 1. *Alkoxyamines* **A** *and* **B**

Experimental. – The synthesis and the properties of nitroxide radicals **11** [26], **12** [27], and **14** and **15** [28] have been described elsewhere. The radicals were analytically pure. *α,α′*-Dimethyldibenzyl ketone (=2,4-diphenylpentan-3-one) and dicumyl ketone (=2,4-dimethyl-2,4-diphenylpentan-3-one; purity > 98%) were prepared according to [29]. The solvent (*tert*-butyl)benzene (*Fluka*; > 99%) was distilled once before use.

For the determination of the cross-reaction rate constants, 1-phenylethyl and cumyl radicals were produced by laser flash photolysis (308 nm) of the corresponding ketones in solutions containing the nitroxide radicals, and their decay was monitored over time at λ 321 nm. All the details of the technique has been described earlier [23].

Results. – Cross-coupling rate constants k_c were measured for a number of structurally related alkoxyamines, *i.e.*, for the nitroxide radicals **1**–**19** (*Table 1*). The rate constants were found to be clearly dependent on the substituent pattern at the C(α) atoms shielding the NO group. The data showed, that k_c was decreasing with increasing steric demand of the substituents. The cross-coupling rate constants k_c of the reaction of **17**, **18**, and **4** with the cumyl radical illustrates another effect (*Table 1*). The two spiro-cyclohexane moieties in the *α,α′*-positions of the piperidinyloxy moiety of **17** were assumed to be bulkier than the four Me groups of TEMPO (=2,2,6,6-tetramethylpiperidin-1-yloxy; **4**). Therefore, one would expect a smaller k_c for **17** than for TEMPO ($k_c = 5.2 \cdot 10^7$ M^{-1} s^{-1}) [23]. In fact, k_c for **17** is two times larger than that for TEMPO, which exemplifies well the importance of the polar effect of electron-withdrawing groups (keto group of **17**, $\sigma_{\text{I,CH}_2\text{COCH}_2} = 0.11$) attached to the nitroxide moiety. This is confirmed by the very similar k_c for **18** and **19** ($k_c = 1.1 \cdot 10^7$ M^{-1} s^{-1}) [23], where the four Ph groups of **18** are expected to be bulkier than the four Et groups of **19**. Indeed, the electron-withdrawing capacity ($\sigma_{\text{I,Ph}} = 0.12$) of the Ph group – larger than the one of Et group ($\sigma_{\text{I,Et}} = -0.01$) – balances the bulkiness of the Ph groups which hamper the approach to the reactive center. The polar effect is likely to disfavor the mesomeric form **D** with respect to form **C** (*Scheme 2*), *i.e.*, facilitating the relocation of the odd electron onto the O-atom of the nitroxide moiety, and, hence, increasing k_c. Therefore, the polar and stabilization effect cannot be separated into elementary components.

Scheme 2. *Mesomeric Forms* **C** *and* **D** *of the Nitroxide Radical*



The cross-coupling rate constants k_c for **11**, **12**, **14**, and **15** with the 1-phenylethyl radical were measured at 296, 323, and 373, or 393 K (*Table 1*). As already observed, k_c increases only very little with the temperature [22][23][30]. For **11**, **12**, and **14**, for which the steric effect is expected to be constant, k_c decreases weakly along the series in parallel with the decreasing electron-withdrawing capacity [31] of the substituent ($\sigma_{\text{I,MeCHC(O)CH}_2} = 0.10$, $\sigma_{\text{I,MeCHCH(OAc)CH}_2} = 0.04$, $\sigma_{\text{I,MeCHCH(OH)CH}_2} = 0.02$), in line with the observations done for **17** and **18**.

However, for nitroxide radicals **1**–**16**, a shotgun-like plot is observed for log k_c *vs.* σ_I (*Fig. 2*, *Table 1*). On the other hand, the plot of log k_c *vs.* E_s (*Fig. 3*, *Table 1*) is linear for **3**, **5**, **8**–**10**, **13**, and **16**, as already reported [31]. The downward deviations for nitroxide

Table 1. *Cross-Coupling Rate Constants* k_c *for the 1-Phenylethyl Radical* (MeCH(Ph)$^\bullet$)a) *and Nitroxide Radicals* **1**–**16** *in* (tert-*Butyl)benzene at Various Temperatures, and the Corresponding Electrical* Hammett *Constants* $\sigma_{I,n}$ *and Modified* Taft *Steric Constants* $E_{s,n}$. *Cross-Coupling Rate Constants* k_c *for the Cumyl Radical* (Cum)b) *and Nitroxide Radicals* **4** *and* **17**–**19** *in* (tert-*Butyl)benzene at Various Temperatures*

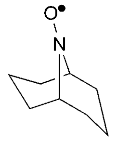
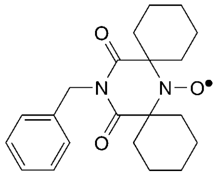
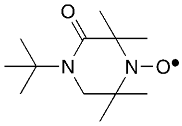
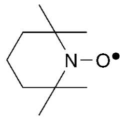
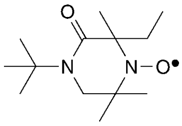
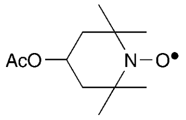
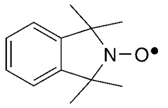
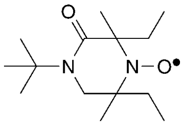
Nitroxide radical		Alkyl radical	k_c(296 K)c)/ 10^7 M^{-1} s^{-1}	k_c(323 K)c)/ 10^7 M^{-1} s^{-1}	k_c(373 K)c)/ 10^7 M^{-1} s^{-1}	$\sigma_{I,n}$d)	$E_{s,n}$e)	Ref.
1		MeCH(Ph)$^\bullet$	43.0f)g)	–h)	–h)	–0.04i)	–2.94j)	[22]
2		MeCH(Ph)$^\bullet$	26.0f)k)	–h)	–h)	0.52l)	–4.20m)	[25]
3		MeCH(Ph)$^\bullet$	26.0	29.0	30.0	0.33	–4.20	[24]
4		MeCH(Ph)$^\bullet$	22.0f)	23.0	–h)	–0.06	–4.20	[22] [23]
5		MeCH(Ph)$^\bullet$	19.0	21.0	22.0	0.33	–4.45	[24]
6		MeCH(Ph)$^\bullet$	17.0f)n)	–h)	–h)	0.00	–4.20	[25]
7		MeCH(Ph)$^\bullet$	15.0f)o)	–h)	–h)	0.08	–4.20	[24]
8		MeCH(Ph)$^\bullet$	12.0	14.0	15.0	0.33	–4.70	[24]

Table 1 (cont.)

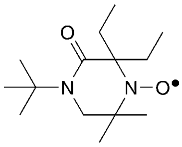
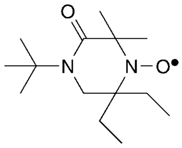
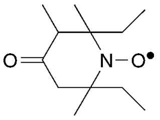
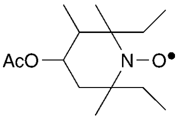
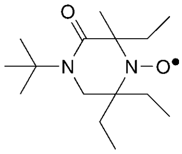
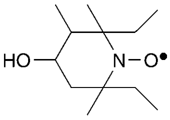
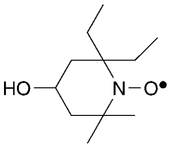
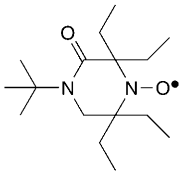
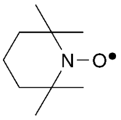
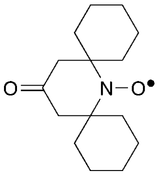
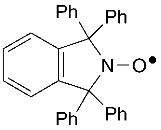
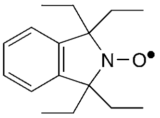
Nitroxide radical		Alkyl radical	k_c(296 K)^c)/ 10^7 M^{-1} s^{-1}	k_c(323 K)^c)/ 10^7 M^{-1} s^{-1}	k_c(373 K)^c)/ 10^7 M^{-1} s^{-1}	$\sigma_{I,n}$^{d})	$E_{s,n}$^{e})	Ref.
9		MeCH(Ph)$^\bullet$	10.0	11.0	11.0	0.33	–5.21	[24]
10		MeCH(Ph)$^\bullet$	10.0	11.0	11.0	0.33	–5.21	[24]
11		MeCH(Ph)$^\bullet$	8.7	10.0	12.0(10)	0.06	–4.70	this work
12		MeCH(Ph)$^\bullet$	8.1	9.3	10.0(10)	0.00	–4.70	this work
13		MeCH(Ph)$^\bullet$	6.8	7.8	8.6	0.33	–5.45	[24]
14		MeCH(Ph)$^\bullet$	6.1^n)	7.1	7.7(2)^p)	–0.02	–4.70	this work
15		MeCH(Ph)$^\bullet$	5.8	6.4	6.7(2)^p)	–0.01	–5.21	this work
16		MeCH(Ph)$^\bullet$	4.0	5.6	5.6	0.33	–6.20	[24]
4		Cum$^\bullet$	5.2	5.7	5.5^p)	–0.06	–4.20	[22][23]

Table 1 (cont.)

Nitroxide radical	Alkyl radical	k_c(296 K)[c])/ 10^7 M^{-1} s^{-1}	k_c(323 K)[c])/ 10^7 M^{-1} s^{-1}	k_c(373 K)[c])/ 10^7 M^{-1} s^{-1}	$\sigma_{I,n}$[d])	$E_{s,n}$[e])	Ref.
17 	Cum$^\bullet$	11.0(10)	12.0(10)	14.0(10)[p])	–[q])	–[q])	this work
18 	Cum$^\bullet$	1.5(2)[n])	1.7(4)	2.6(4)[p])	–[q])	–[q])	this work
19 	Cum$^\bullet$	1.1	1.2	0.9[p])	–[q])	–[q])	[23]

[a]) MeCH(Ph)$^\bullet$ = 1-phenylethyl radical. [b]) Cum$^\bullet$ = cumyl radical = 1-methyl-1-phenylethyl radical. [c]) Errors given in parentheses on the last unit. [d]) Given by *Eqn. 2* and those in [15] [31] [32]. [e]) Given by *Eqns. 3* and *4*, see text; r_i(H) = 0.32, r_i(Me) = 0.0, r_i(Et) = − 0.38, see [33]. [f]) At 293 K. It was assumed that the difference of temperature was not significant. [g]) Given in isooctane (= 2-methylheptane), $k_c = 86.0 \cdot 10^7$ M^{-1} s^{-1}. [h]) Not measured. [i]) $\sigma_{I,H} = 0$, $\sigma_{I,Me} = -0.01$, see [32]. [j]) It was assumed that the rings out of the nodal plane were not more sterically demanding than the Me group. [k]) Measured in MeCN, $k_c = 15.0 \cdot 10^7$ M^{-1} s^{-1}. [l]) It was assumed [31] that $\sigma_{I,(PhCH_2)(Me)NCO} \approx \sigma_{I,Me_2NCO} = 0.28$. [m]) It was assumed that the spiro-cyclohexane rings in positions α,α' were not more sterically demanding than the Me group due to the peculiar conformation of the ring generated by the presence of two sp^2 C-atoms [31]. [n]) Measured in MeCN, $k_c = 9.8 \cdot 10^7$ M^{-1} s^{-1}. [o]) Measured in isooctane, $k_c = 30.0 \cdot 10^7$ M^{-1} s^{-1}. [p]) Measured at 393 K. [q]) Not given.

radicals **1**, **6**, **7**, **11**, **12**, and **15** are likely due to the polar/stabilization effect. Therefore, as for the case of the homolysis, the variation of log k_c should be described by *Eqn. 1* with the electrical *Hammett* constant [32] $\sigma_{I,\mathbf{n}}$ accounting for the stabilization/polar effect [15] [31] and the modified *Taft* steric constant [33] $E_{s,\mathbf{n}}$ accounting for the congestion around the nitroxide moiety [15] [31]. The values of $\sigma_{I,\mathbf{n}}$, which is the sum of the σ_I values for each substituent, and $E_{s,\mathbf{n}}$ (*Fig. 4*) are given by *Eqns. 2–4* and presented in *Table 1*. It has to be mentioned that the larger the group R$_i$, the smaller r_i, thus r_1 corresponds to the small size group, r_2 to the medium size group, and r_3 to the large size group.

$$\log(k_{c,\mathbf{n}}/\text{M}^{-1}\,\text{s}^{-1}) = \log(k_{c,0}/\text{M}^{-1}\,\text{s}^{-1}) + \rho_I \cdot \sigma_{I,\mathbf{n}} + \delta \cdot E_{s,\mathbf{n}} \tag{1}$$

$$\sigma_{I,\mathbf{n}} = \sum_{i=1}^{6} \sigma_I(\text{R}_i) \tag{2}$$

$$E_{s,\mathbf{n}} = E^{A}_{s,\boldsymbol{n}} + E^{B}_{s,\boldsymbol{n}} \tag{3}$$

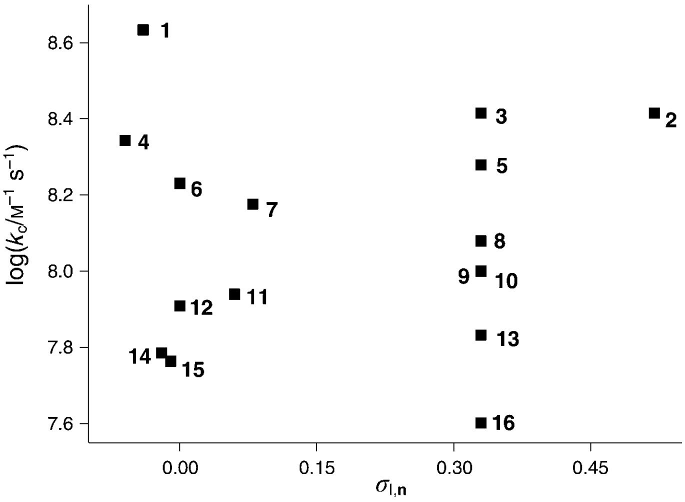


Fig. 2. *Plot of log(*k$_c$/M^{-1} *s*$^{-1}$*)* vs. $\sigma_{I,n}$ *for molecules* **1**–**16**

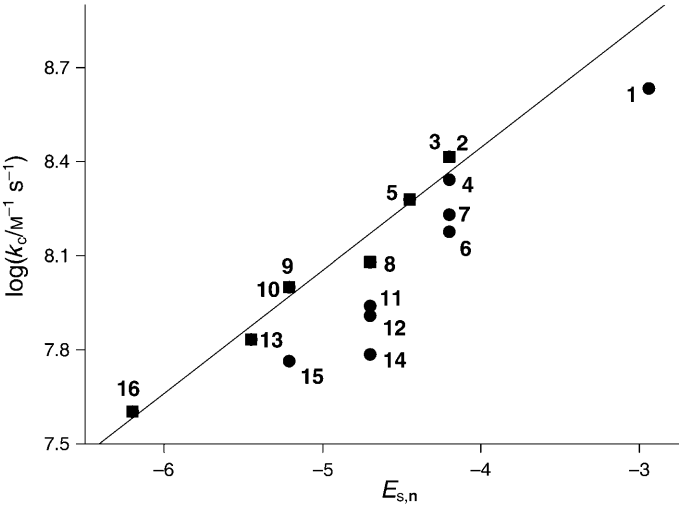
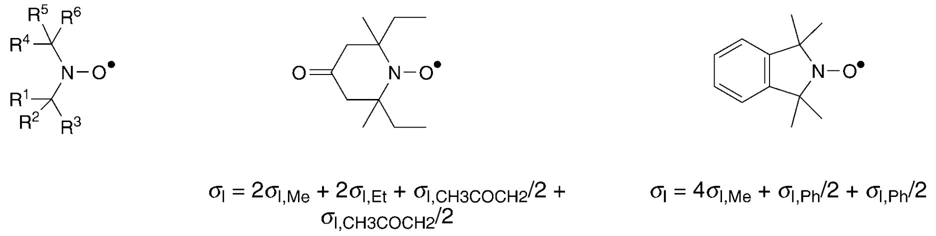


Fig. 3. *Plot of log(*k$_c$/M^{-1} *s*$^{-1}$*)* vs. $E_{s,n}$ *for molecules* **1**–**16**. ■: Data for nitroxide radicals **3**, **5**, **8**–**10**, **13**, and **16**; ●: data for **1**, **2**, **4**, **6**, **7**, **11**, **12**, **14**, and **15**.

$$E_{s,n}^{\mathrm{A\ or\ B}} = -2.104 + 3.429 \cdot r_1(\mathrm{R}_1) + 1.978 \cdot r_2(\mathrm{R}_2) + 0.649 \cdot r_3(\mathrm{R}_3) \quad (4)$$

For the homolysis of the alkoxyamines corresponding to the nitroxide radicals listed in *Table 1*, k_d exhibited a strong dependence on the ring conformation [31]. Assuming that the steric constants E_s determined for the cyclic nitroxide moiety of alkoxyamines hold for nitroxide radicals, *Eqn. 1* was applied, and yielded (*Eqn. 5*, *Table 2*) not quite good statistical values. The slope for the steric effect ($\delta = 0.29$) was different from the one previously [24] determined ($\delta = 0.36$) for **3**, **5**, **8**–**10**, **13**, and **16**. Therefore, the ring



$\sigma_I = 2\sigma_{I,Me} + 2\sigma_{I,Et} + \sigma_{I,CH3COCH2}/2 + \sigma_{I,CH3COCH2}/2$

$\sigma_I = 4\sigma_{I,Me} + \sigma_{I,Ph}/2 + \sigma_{I,Ph}/2$

Fig. 4. *Examples of polar/stabilization and steric effects in nitroxide radicals*

Table 2. *Parameters* ρ *and* δ, *and Statistical Outputs for* Eqn. 1 *Applying* $E_{s,n}$ *Given in* [15][31] (*Eqn. 5*), *and Applying New Estimated* $E_{s,n}$ (*Eqns. 6* and *7*)

Eqn.	log k_{c0}^{a})	ρ_I^{a})	δ^{a})	N^{b})	R^2 ^{c})	s^{d})	t^{e})	F_N^{f})
5^{g})	8.97(17)	0.88(26)	0.29(5)	14^{h})	0.75	0.13	99.40^{i}) 99.98^{j})	16^{k})
6^{g})	9.85(15)	0.57(13)	0.40(3)	16	0.91	0.09	99.92^{i}) 99.99^{j})	68^{l})
7^{m})	9.82(26)	0.66(18)	0.38(5)	12^{n})	0.85	0.10	99.50^{i}) 99.99^{j})	26^{o})

^{a}) Errors in parentheses given on the last digit. ^{b}) Number of data. ^{c}) Square of the linear regression coefficient. ^{d}) Standard deviation. ^{e}) Student *t*-test. ^{f}) *F*-Test. ^{g}) At 296 K. ^{h}) $E_{s,n}$ values were not available for **1** and **2**. ^{i}) *t*-Test for ρ_I. ^{j}) *t*-Test for δ. ^{k}) *F*-Test at 0.05%. ^{l}) *F*-Test at 0.01%. ^{m}) At 323 K. ^{n}) Values of k_c for **1**, **2**, **6**, and **7** were not available. ^{o}) *F*-Test at 0.02%.

does not have the same influence on k_c than on k_d. Thus, it was assumed that the cyclic strain exerts no significant influence on the congestion around the nitroxide moiety. Then, it was assumed that whatever the ring size – five- or six-membered rings – and substituents at the positions other than the positions α and α', the ring exhibited the same steric demand for all molecules presented in *Table 1*. For the sake of simplicity, it was assumed that the groups or ring on the nodal plane of the nitroxide moiety exhibited identical steric demand than the Me group, and thus, the r values of these groups/rings were taken as r_1 and equal to zero [34]. Finally, applying *Eqns. 1–4* to molecules **1**–**16** yielded *Eqns. 6* (T 296 K) and *7* (T 323 K) with good statistical outputs (*Table 2*). Regression parameters were improved when molecules **4** and **14** were removed. The upward deviation of **4** is due to a k_c value two times higher than expected from *Eqn. 6*. The downward deviation of **14** is due to a k_c value 1.5 times lower than expected from *Eqn. 6*. It is worthy to mention that the y-intercept (log $k_{c,0}$) corresponds to the typical value of k_c observed for diffusion-controlled reactions.

Discussion. – As mentioned above, the scavenging of the cumyl radical by **17** and **18** emphasizes well the polar effect due to the presence of electron-withdrawing groups (EWGs) close to the nitroxide moiety. That is, bulky groups such as phenyl or spiro-cyclohexane groups hamper the approach of the cumyl radical to the nitroxide moiety and thus decrease k_c, whereas the presence of an EWG attached to the nitroxide moiety balances or overbalances the steric effect as for **18** and **19** and as for **17** and

TEMPO, respectively (see *Results*). In fact, EWGs destabilize the form **D** in favor of form **C**, and thus facilitate the relocation of the odd electron onto the O-atom of the nitroxide function (*Scheme 2*). Hence, the polar and stabilization effects cannot be studied separately. However, this should not be the case for a nitroxide moiety carrying aromatic or vinylic fragments, *i.e.*, π-system attached to the nitroxide moiety, for which strong delocalization of the odd electron should be observed independently of the presence of EWG. Such a trend is also observed for the scavenging of the 1-phenylethyl radical by nitroxide radicals **1**–**16**. Thorough studies of rate constants k_d for the C–ON bond homolysis showed that the steric effect was strongly dependent on the size of the ring, on the substituents, and on the hybridization of the atoms of the ring [15][31]. On the other hand, for the re-formation of the alkoxyamine, k_c does not depend on the ring size or on the ring substituents, as shown by the poor regression (*Eqn. 5*, *Table 2*) obtained with the E_s values applied to k_d. Thus, a bi-parameter correlation (σ_I and E_s) was performed, and the expected straight line was observed (*Eqn. 6* in *Table 2*, *Fig. 5*). By using the weighting equations [16][35], the polar/stabilization and steric effects are given at 27% and 73%, respectively, for *Eqn. 6* at 296 K, at 35% and 65%, respectively, for *Eqn. 7* at 323 K. Hence, the polar/stabilization effect is the minor effect (*ca.* 30%) although still important. As already mentioned [24], the steric effects for the re-formation and the homolysis of the C–ON bond are anti-correlated, as shown by the positive sign (*Eqn. 6*, *Table 2*) for δ and the negative sign for δ_d (*Eqn. 8*) [15][31], respectively. And, as expected, the polar/stabilization effects for the re-formation and the homolysis of the C–ON bond are anti-correlated, as shown by the positive sign for ρ_I (*Eqn. 6*, *Table 2*) and the negative sign for $\rho_{I,d}$ (*Eqn. 8*) [15][31], respectively. The positive sign for the steric parameter means that the reaction is retarded by the increasing size of the substituents attached to the nitroxide moiety, that is, in the tran-

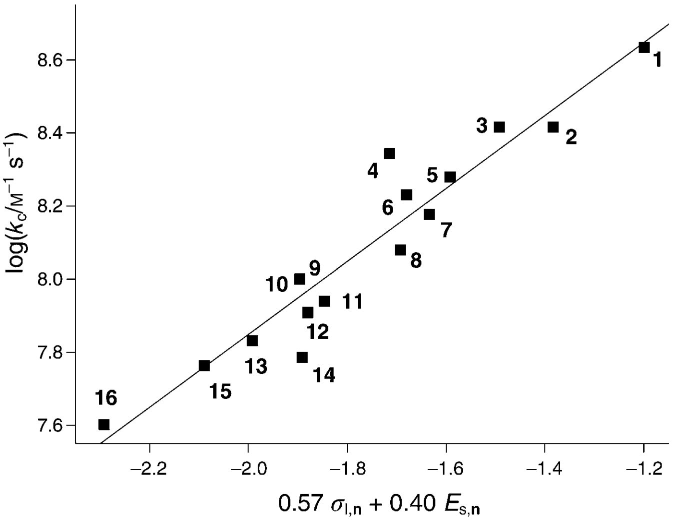


Fig. 5. *Log*(k_c/M^{-1} s^{-1}) vs. Eqn. 1 *at 293 K for molecules* **1**–**16**

sition state (TS), the approach of the alkyl radical to the reactive center is hampered by bulky groups, *i.e.*, the TS is destabilized. The positive sign of the polar/stabilization parameter means that the reaction is accelerated by increasing the electron-withdrawing capacity of the substituents attached to the nitroxide moiety. The presence of EWGs destabilizes the nitroxide moiety, thereby, destabilizing the initial state and thus TS, by virtue of the *Hammond* principle. However, the destabilizing effect of EWGs is overmatched by the relocation of the odd electron onto the O-atom of the nitroxide moiety, *i.e.*, the increased weight of form **C**, which makes the coupling easier in the TS. As the polar/stabilization and steric constants were estimated in the same way for both the re-formation and the homolysis of the C–ON bond, the comparison of the absolute values of the parameters was made possible. It comes out that the re-formation reaction is roughly two times less sensitive to the size of the substituents and roughly 5 times less sensitive to the electron-withdrawing capacity of the substituents than the homolysis is.

$$\log(k_\mathrm{d}/\mathrm{s}^{-1}) = -5.73 - 2.81 \cdot \sigma_\mathrm{I} - 0.83 \cdot E_\mathrm{s} \tag{8}$$

Conclusions. – Like the rate constants k_d for the homolysis of the alkoxyamines C–ON bond, the rate constants k_c for the re-formation of the C–ON bond are well accounted for by the polar/stabilization and steric effects. Hence, with *Eqn. 6*, it is possible to predict the values of k_c at first glance on the structure. To apply *Fischer*'s phase diagrams [7] [9], it is now possible to know the values of k_d and k_c by combining the relationships developed in this work and in the literature. Such diagrams are very useful to determine the fate of NMP.

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