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Chemically Triggered C−ON Bond Homolysis of Alkoxyamines. 5. Cybotactic Effect

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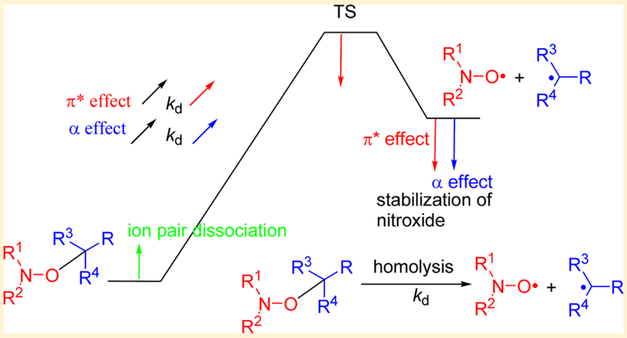
Supporting Information



ABSTRACT: In a recent work (*Org. Lett.* **2012**, *14*, 358), we showed that the rate constant k_d of the chemically activated C−ON bond homolysis of alkoxyamines was subject to solvent effects. However, we showed that solvent effects were weak for the nonactivated alkoxyamine **1** (diethyl (1-(*tert*-butyl(1-(pyridin-4-yl)ethoxy)amino)-2,2-dimethylpropyl)phosphonate) and its $N^+—O^-$ oxide activated version **3**. On the other hand, the activated *N*-methylated version **2** of **1** experienced a strong solvent effect for a radical reaction, i.e., a 24-fold increase in k_d from *tert*-butylbenzene (*t*BuPh) to 2,2,2-trifluoroethanol (TFE). Good correlations were observed with the normalized Reichardt solvent polarity constant E_T^N and the nitrogen hyperfine coupling constant of the released nitroxide $a_{N,SG1}$, meaning that the stabilization of the nitroxide played an important role in C−ON bond homolysis in alkoxyamines. The Kalmet−Abboud--Taft relationships described successfully the solvent effect for each diastereoisomer of **1** and **2**, as for example with the minor diastereoisomer of **1** $\log(k_d'/s^{-1}) = -4.84 + 0.37\pi^* + 0.21\alpha$ and that of **2** $\log(k_d'/s^{-1}) = -3.11 + 0.37\pi^* + 0.47\alpha$, with π^* being the polarity/polarizability and α the hydrogen bond donor (HBD) ability of the solvent. Surprisingly, the HBD effect is larger for **2** than for **1**, whereas no extra lone pair is available in **2**. This amazing effect was ascribed to the solvation of the counteranion, which is expected to be better solvated in a HBD solvent.

INTRODUCTION

Since the pioneering work of Rizzardo[1] and the seminal work of Georges,[2] nitroxide-mediated polymerization (NMP) has become a mature technology which is applied everyday in academic laboratories and factories to prepare new materials.[3] The NMP process is generally described as a three-stage process, as for conventional polymerization (Scheme 1):[4] initiation stage, propagation stage, and termination stage, with both conventional termination of alkyl radicals and specific termination reactions due to the nitroxide/alkoxyamine couple.

Recently, we developed the chemical triggering of the C−ON bond homolysis of alkoxyamines and observed amazing solvent effects.[5,6] To the best of our knowledge, only three studies dealing with the solvent effects on the C−ON bond homolysis have been reported over the last 25 years, and the two oldest ones dealt with 6−7 solvents without covering all properties of solvent,[9,10] and recently[8] we investigated the cybotactic effect[11−13] of 15 solvents covering the main effects: i.e., polarity/polarizability, solvation, intermolecular hydrogen bonding, size, stabilization of the nitroxide, etc. In the same period, Zaremski et al.[14] reported the solvent effects for several macro-alkoxyamines and did not observe a striking effect of the solvent on the k_d values, in nice agreement with our previous reports,[8,10] except for poly(acrylic acid)-SG1 based alkoxyamines, which exhibited a 20-fold larger k_d value in formamide than in dioxane. Other investigations with few solvents[15,16] or in NMP[17−20] are also available. However, these studies were focused on alkoxyamines which were not prone to solvent effects: i.e., no possibility for strong hydrogen bonding occurrence, weakly polar alkyl fragment on alkoxyamine, etc. In this report, we investigate the effect of 15 solvents, covering the main effects with alkoxyamine **2** (Figure 1), which is activated by the *N*-methylation of **1** ($k_{d,2} \approx 24k_{d,1}$). We show that the cybotactic effect[11−13] can be mainly ascribed to the stabilization of the nitroxide for **1** and **2** and that the unexpected and amazing effect observed with HBD solvents can be ascribed to the solvation of the counterion: that is, replacing a nonpolar solvent by a hydrogen bond donor (HBD) solvent induces the dissociation of the intimate ion pair into an separate ion pair.

RESULTS

Alkoxyamine **2** is not soluble in *n*-octane. A few examples of semilog plots $\ln(C/C_0)$ vs t are displayed in Figure 2 for **2**. k_d values for **2** are gathered in Table 1. The selected parameters for the correlations, i.e., the normalized Reichardt solvent polarity parameter E_T^N,[12] the nitrogen hyperfine coupling constants $a_{N,TEMPO}$ and $a_{N,SG1}$ of 4-amino TEMPO[21] and SG1,[22] respectively, the intrinsic volume V_X as given by McGowan,[23,24] the hydrogen bond donor (HBD) α property,[12,25] the polarity/polarizability parameter π^*,[12,26] the dipolar moment μ,[12] the dielectric constant ε_r,[26] the viscosity η,[12] the hydrogen bond acceptor (HBA) β

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Scheme 1. Kinetic Scheme for NMP[a]

Initiation

$R^1R^2NOR \longrightarrow R^1R^2NO^\cdot + {}^\cdot R$ k_d

$R^1R^2NO^\cdot + {}^\cdot R \longrightarrow R^1R^2NOR$ k_c

$R^\cdot + M \longrightarrow R{-}M_1^\cdot$ k_{add}

Propagation

$R^1R^2NO^\cdot + {}^\cdot RM_n \longrightarrow R^1R^2NOM_nR$ $k_{c,ds}$

$R^1R^2NOM_nR \longrightarrow R^1R^2NO^\cdot + {}^\cdot RM_n$ $k_{d,ds}$

$RM_n^\cdot + nM \longrightarrow RM_n^\cdot$ k_p

Termination

Self-termination

$R^\cdot + RM_n^\cdot \longrightarrow$ dead products $k_{t,ds}$

Cross side-reactions

$R^1R^2NOR \longrightarrow R^1R^2NOH$ + alkene k_{dD}

$R^1R^2NO^\cdot + R^\cdot \longrightarrow R^1R^2NOH$ + alkene k_{cD}

$R^1R^2NO^\cdot + (R^\cdot) \longrightarrow X$ k_{dec}

[a] Legend to stages: initiation stage, with the rate constants k_d and k_c for the homolysis and reformation of the C−ON bond of the initiator, respectively, and with the initiation rate constant k_{add} of the polymerization; propagation stage, with the rate constants $k_{d,ds}$ and $k_{c,ds}$ for the homolysis and re-formation of the C−ON bond of the dormant species ds (macro-alkoxyamine), respectively, and with the propagation rate constant k_p; termination stage, with the self-termination rate constants k_t for alkyl radicals (initiating and propagating alkyl radicals) and side reactions such as intramolecular proton transfer (IPT, k_{dD}), intermolecular hydrogen atom transfer (IHAT, k_{cD}), and CO−N bond homolysis. Reproduced by the permission of The Royal Society of Chemistry, http://pubs.rsc.org/doi:10.1039/c0cs00110d.

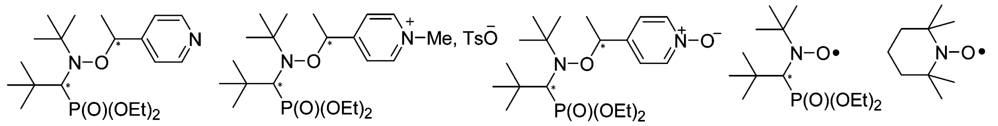
property,[12,27] the cohesive pressure c,[12,26] the molar volume V_M,[26] the refractive index n,[26] and the solvent basicity parameter B as given by Koppel−Palm[26] are provided as Supporting Information (Table 1SI). Previously reported experimental data for **1** are given in Table 2SI[8] in the Supporting Information.

Correlations with Nonspecific Properties of the Solvent. As reported for **1**,[8] conventional solvent parameters such as μ, ε_r, η, and n showed only scattered plots (not reported) for **2**. Multiparameter correlations of these parameters did not improve the plots and the statistics.

Correlations with Cybotactic Parameters. As the nonspecific solvent properties (μ, ε_r, η, and n) were not suitable to describe the reactivities reported, several cybotactic parameters were investigated. As reported for **1**,[8] c (square of the Hildebrand solubility parameter δ_H) and α afforded scattered plots with **2**. On the other hand, for **2**, as already reported for **1**,[8] V_X afforded good correlations ($R^2 > 0.8$), which highlights the organization of the first solvent layer around the products and the reactants; the moderate correlations ($R^2 > 0.7$, Tables 2 and 3) obtained for E_T^N suggested an influence of the polarity of the solvent although it did not account for all of the reactivity; moderate correlations ($R^2 < 0.8$, Tables 2 and 3) were observed with both the $a_{N,TEMPO}$ and $a_{N,SG1}$values.[28,29]

Hence, as for **1**,[8] the negative slopes for V_X and the positive slopes for E_T^N, $a_{N,TEMPO}$, and $a_{N,SG1}$ implied that the solvent effect both at TS and on products overmatched its effect on the starting materials. The moderate correlations observed for $a_{N,TEMPO}$ and $a_{N,SG1}$ mean that the stabilization of the release nitroxide played a role on the increase in the reactivity. Interestingly, the two times larger slopes observed for **2** than for **1** (eqs 6−9 and 14−16, Tables 2 and 3) mean that $a_{N,TEMPO}$ and $a_{N,SG1}$ did not probe the same effect in **1** and in **2** (vide infra). Interestingly, the two diastereoisomers of **2** did not experience the same cybotactic effect, as the diastereomeric ratio of the homolysis rate constants $k_{d,mino}/k_{d,majo}$ exhibited 9 in 14 values larger than 1.44,[30] spanning from 1.5 (2 and 12) to 3.18 (10).[30] Interestingly, DCE solvent was an outlier for all plots, TEG was an outlier because E_N^T does not describe all effects, and the outlier *t*-BuPh/MeOH mixture means that a_N values do not describe all effects involved.

Correlations with the Koppel−Palm[12,26] and the Kalmet−Abboud−Taft[12] Relationships. Solvent effects are often investigated using the Koppel−Palm[31] (KP) and



1 **2** **3** **SG1** **TEMPO**

Figure 1. Alkoxyamines investigated and structures of SG1 and TEMPO nitroxides.

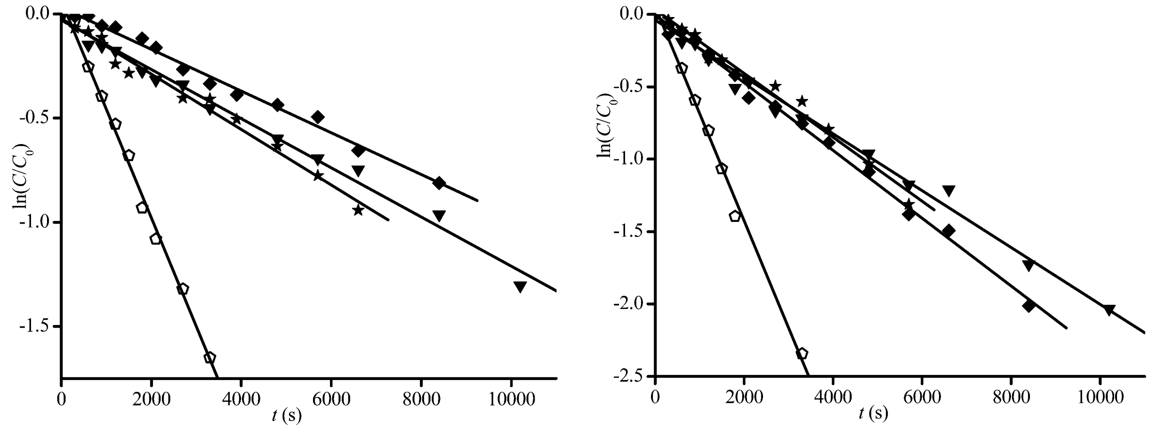


Figure 2. Plots of ln(C/C_0) vs t for DMSO (▼), formamide (♦), DMF (★), and TFE (⬠) as solvents for the minor (left) and major (right) diastereoisomers of **2** at 40 °C.

Table 1. k_d Values and Activation Energies E_a Measured for Solvents 2–15 and Their Re-Estimated k_d' Values at 60 °C for the Minor and Major Diastereoisomers of 2

		minor isomer (*RR/SS*)[a]				major isomer (*RS/SR*)[a]		
	solvent	T (°C)	k_d (10^{-4} s^{-1})[b]	E_a(kJ/mol)[c,d]	k_d' (10^{-3} s^{-1})[e]	k_d (10^{-4} s^{-1})[b]	E_a(kJ/mol)[c,d]	k_d' (10^{-3} s^{-1})[e]
1	octane	*f*	*f*	*f*	*f*	*f*	*f*	*f*
2	*n*-Bu_2O	60	9.4	111.0	0.9	4.6	112.9	0.5
3	TEG	40	0.5	111.9	0.7	0.7	111.1	0.7
4	*t*-BuPh	60	7.4	111.6	0.7[g]	5.2	112.6	0.6[g]
5	*t*-BuOH	40	1.1	109.9	1.4	0.6	111.5	0.8
6[h]	*t*-BuPh/CH_2Cl_2 (v/v 1/1)	*f*	*f*	106.6	4.6	*d*	108.0	2.7
7	NMF	40	2.4	107.9	2.8	1.6	108.9	2.0
8	DMF	40	2.2	108.1	2.6	1.3	109.5	1.6
9	EtOH	60	40.0	107.0	4.2[i]	30.0	107.8	3.0[i]
		40	3.7	106.7		2.5	107.7	
10	DCE	40	11.0	103.9	12.1	3.3	107.3	3.5
11	DMSO	40	1.9	108.5	2.3	1.2	109.7	1.5
12	Formamide	40	2.3	108.0	2.7	1.0	110.1	1.3
13[h]	H_2O/MeOH (v/v 1/1)	*f*	*f*	106.1	5.5	*f*	107.8	3.0
14	TFE	40	11.0	103.9	12.1	4.8	106.1	5.5
15	water	40	4.1	106.5	4.7	3.2	107.1	3.8

[a] As defined in ref 5. [b] Statistical errors are less than 2%. [c] Estimated using the average value of $A = 2.4 \times 10^{14}$ s^{-1}.[4,34] [d] Commonly accepted errors are given as ±1 kJ/mol. [e] Estimated using the frequency factor given in footnote *b* combined with data in the fifth column for the minor isomer and with those in the eight column for the major isomer. [f] Not measured. See text. [g] Given by the average of values reported in ref 7: E_a = 111.7 and 113.2 kJ/mol for minor and major diastereoisomers, respectively. [h] Given in ref 7. [i] Given using the average of E_a estimated at 40 and 60 °C.

Table 2. Linear Correlations $y = a + bx$ for $\log(k_d'/s^{-1})$ vs Cybotactic Parameters (V_X, E_T^N, $a_{N,TEMPO}$, and $a_{N,SG1}$) in Various Solvents at 60 °C for the Minor Diastereoisomers of 1 and 2 and Their Subsequent Statistical Outputs

eq	alkoxyamine	param	*y* intercept[a]	slope[a]	R^2 [b]	N[c]	SD[d]	outliers[e]
1	**1**[f]	V_X	−4.25(5)	−0.0044(5)	0.87	11	0.06	14
2	**2**	V_X	−2.21(6)	−0.0072(8)	0.92	10	0.09	10, 14
3	**1**[f]	E_T^N	−4.81(7)	0.54(12)	0.79	12	0.10	3
4	**2**	E_T^N	−3.18(12)	1.07(20)	0.76	11	0.19	3, 10
5	**1**[f]	$a_{N,TEMPO}$	−10.34(90)	0.36(6)	0.77	14	0.10	none
6	**2**	$a_{N,TEMPO}$	−12.05(179)	0.59(11)	0.74	12	0.21	6, 10
7	**1**[f]	$a_{N,SG1}$	−11.81(78)	0.52(6)	0.88	13	0.08	11
8	**2**	$a_{N,SG1}$	−15.43(226)	0.91(17)	0.77	12	0.20	6, 10, 15

[a] Error given in the last digit. [b] Square of the linear regression coefficient. [c] Number of data. [d] Standard deviation. [e] Outliers displayed in Figure 3. [f] Values given in ref 8.

Table 3. Linear Correlations $y = a + bx$ for $\log(k_d'/s^{-1})$ vs Cybotactic Parameters (V_X, E_T^N, $a_{N,TEMPO}$, and $a_{N,SG1}$) in Various Solvents at 60 °C for the Major Diastereoisomers of 1 and 2 and Their Subsequent Statistical Outputs

eq	alkoxyamine	param	*y* intercept[a]	slope[a]	R^2 [b]	N[c]	SD[d]	outliers[e]
9	**1**[f]	V_X	−4.17(7)	−0.0050(8)	0.85	11	0.08	12
10	**2**	V_X	−2.35(10)	−0.007(1)	0.83	9	0.14	10, 12, 14
11	**1**[f]	E_T^N	−4.80(7)	0.53(13)	0.62	12	0.13	3
12	**2**	E_T^N	−3.33(8)	1.05(13)	0.88	10	0.13	3, 10, 12
13	**1**[f]	$a_{N,TEMPO}$	−9.90(72)	0.33(5)	0.85	12	0.08	8, 11
14	**2**	$a_{N,TEMPO}$	−10.37(164)	0.47(10)	0.67	12	0.19	6, 10
15	**1**[f]	$a_{N,SG1}$	−10.85(84)	0.45(6)	0.85	12	0.08	8, 11
16	**2**	$a_{N,SG1}$	−11.43(167)	0.61(12)	0.74	11	0.18	6, 9, 10

[a] Error given on the last digit. [b] Square of the linear regression coefficient. [c] Number of data. [d] Standard deviation. [e] Outliers displayed in Figure 3. [f] Values given in ref 8.

Kalmet–Abboud–Taft (KAT) relationships (17a) and (18), respectively.[12,26] However, neither the conventional nor the modified (eq 17b)[8] KP relationships were able to describe the reactivity observed for **2**. On the other hand, solvent effects are described by the Kalmet–Abboud–Taft relationship (18) relying on four cybotactic parameters: the polarity/polarizability

$$\log k'_d = \log k'_{d,0} + a_1 f(n^2) + a_2 f(\varepsilon) + a_3 B + a_4 \delta^2 + a_5 E_T^N + a_6 V_M \tag{17a}$$

$$\log k'_d = \log k'_{d,0} + a_2(\pi^* + d\delta) + a_7 \alpha + b\beta \tag{18}$$

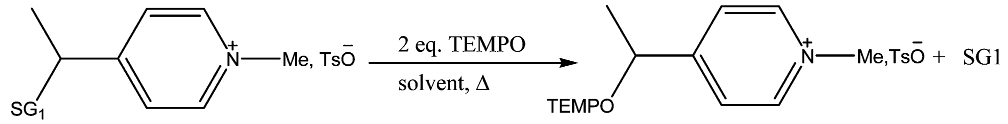
$$\log k'_d = \log k'_{d,0} + a_2 \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} + a_7 a_{N,SG1} \tag{17b}$$

Table 4. Coefficients and Statistical Outputs for the KAT Relationships for 1 and 2

eq		$\log(k_d'/s^{-1})^a$	$a_2{}^a$	*t* test^b	$a_7{}^a$	*t* test^b	$R^{2\,c}$	SD^d	N^e	*F* test^f
19	**1**^{g,h}	−4.90(3)	0.43(5)^{i,j}	99.99	0.23(3)^{i,k}	99.97	0.95	0.05	10	73
20	**1**^{h,l}	−4.94(3)	0.563(4)^{i,m}	99.80	0.17(2)^{i,n}	99.99	0.93	0.04	12	56
21	**2**^{g}	−3.11(14)	0.37(19)^{i,o}	90.31	0.47(11)^{i,p}	99.72	0.82	0.16	10	16^q
22	**2**^{l}	−3.42(9)	0.56(13)^{i,r}	99.62	0.45(9)^{i,s}	99.89	0.92	0.13	10	39^q

[a] Error given on the last digit. [b] Student *t* test. [c] Square of the regression coefficient. [d] Standard deviation. [e] Number of data. [f] Student−Fischer *F* test given at 99.99% confidence level unless otherwise mentioned. [g] Minor diastereoisomer. [h] Given in ref 8. [i] Weight of the coefficient w_X estimated with equations given in ref 34. [j] $w_{\pi*}$ = 53%. [k] w_α = 47%. [l] Major diastereoisomer. [m] $w_{\pi*}$ = 69%. [n] w_α = 31%. [o] $w_{\pi*}$ = 30%. [p] w_α = 70%. [q] 99.85% confidence level. [r] $w_{\pi*}$ = 36%. [s] w_α = 64%.

Scheme 2



term π^*, the discontinuous polarizability correction term δ, the hydrogen bond acceptor HBA (basicity) β, and the hydrogen bond donor HBD (acidity) α properties of the solvent. Indeed, the KAT relationship describes the solvent effect using cybotactic parameters, in contrast to the KP relationship, for which the nonspecific properties of the solvent (n and ε_r) are described by the cybotactic parameter π^*. Statistical analysis showed that neither δ nor β was significant, as **2** did not carry "acidic" protons. Correlations using π^* and α as parameters were moderate for **2** (Table 4).

Interestingly, KAT relationships (Figure 4) performed better than KP relationships, as it was possible to describe the reactivity of **2** using parameters with good statistical significance (Student *t* test and Student−Fischer *F* test, Table 4). The slopes of π^* and α are positive, implying that k_d' increased with polarity/polarizability and HBD properties, whereas the nitrogen lone pair of the pyridyl group was suppressed by the methylation. DCE is still an outlier.

■ DISCUSSION

It is commonly accepted that the solvent effect is generally ascribed to the stabilization of the reactants, TS, and products.[12] Hence, the negative slopes for V_X and the positive slopes for $E_T{}^N$, $a_{N,TEMPO}$, and $a_{N,SG1}$ implied that its effect both at TS and on products overmatched its effect on starting materials. The trends observed for **2** with V_X, $E_T{}^N$, $a_{N,TEMPO}$, and $a_{N,SG1}$ are the same as for **1**, except that the observed effects are 2 times larger for **2**. That is, the negative slopes reported for the plots of log k_d' against V_X point to the products being better solvated by the small molecules than by the large ones; the positive slopes for the plots of log k_d' against $E_T{}^N$ (Figure 3) show that the higher the solvent polarity, the greater the k_d' value, meaning that either TS or products are more stabilized than the starting materials. When the reaction involved a nitroxide, its stabilization often plays an important role and is readily probed by investigating the effect of the solvent polarity on the a_N values: that is, the higher the solvent polarity $E_T{}^N$, the higher the a_N values and, hence, the more stabilized the nitroxide, as the zwitterionic mesomeric form **B** is favored over the nonpolar mesomeric form **A** (Figure 5).[32]

In a recent work,[8] we showed that the KAT relationship was partially able to describe the reactivity reported with **1** and **3**. Interestingly, eq 18 was able to describe the reactivity of both diastereoisomers of **2** using π^* and α (eqs 21 and 22, Table 4). The slopes for the π^* effect are the same for **1** and **2**, meaning that **1** and **2** were stabilized in the same way both at TS and at products, either activated or nonactivated. On the other hand, the α effect is related to both the released alkyl and nitroxyl radicals. As the nitroxides are the same in **1** and **2**, and as the alkyl radical/fragment of **2** has no lone pair, a decrease in k_d was expected, in sharp contrast with the 2 times larger value observed for the slope of **2** than for that of **1**.

However, the activation of **1** by methylation involved the formation of salt: i.e., pyridinium cation **2** and tosylate anion TsO^-. Such an anion is expected to be sensitive both to the polarity/polarizability and to the HBD ability of the solvent. This extra α effect observed can be ascribed to the ability of the solvent to dissociate the ion pair (Figure 6). Hence, in an apolar solvent, an intimate ion pair is expected, involving two charges in close vicinity to one another leading to a partial cancellation of the effect of the charge on the remainder of the molecule, and in a HBD solvent-separated ion pairs are expected, involving separate charges, affording a full effect of the charge on the remainder of the molecule.

■ CONCLUSION

This study shows that the C−ON bond homolysis in alkoxyamines **1** and **2** experiences very different cybotactic effects r_c which depend both on the diastereoisomers and on the alkoxyamine: that is, for the minor and the major diastereoisomers of **1** ($r_c = k'_{d,TFE}/k'_{d,octane}$) from octane to TFE $r_c = 8$ and $r_c = 4$, respectively, whereas for **2** ($r_c = k_{d,TFE}/k_{d,t\text{-}BuPh}$) from *t*-BuPh to TFE $r_c = 13$ and $r_c = 11$, respectively. This means that the two diasteroisomers did not experience the same cybotactic effect and that this effect also depends on the type of alkoxyamine. This observation is even more striking when the solvent effects ($r_s = k_{d,2}/k_{d,1}$) on **1** and **2** are compared: e.g., for the minor diastereoisomer in *n*-octane $r_s = 69$, in TFE $r_s = 190$, in DCE $r_s = 366$, and for the major diastereoisomer $r_s = 50$, $r_s = 77$, and $r_s = 127$, respectively.

Furthermore, the KAT relationship analysis showed that the k_d values depend on the state of the ion pair: i.e. intimate or separate. Such results should open the possibility to initiate a radical reaction by changing the solvent and using moderate temperatures.

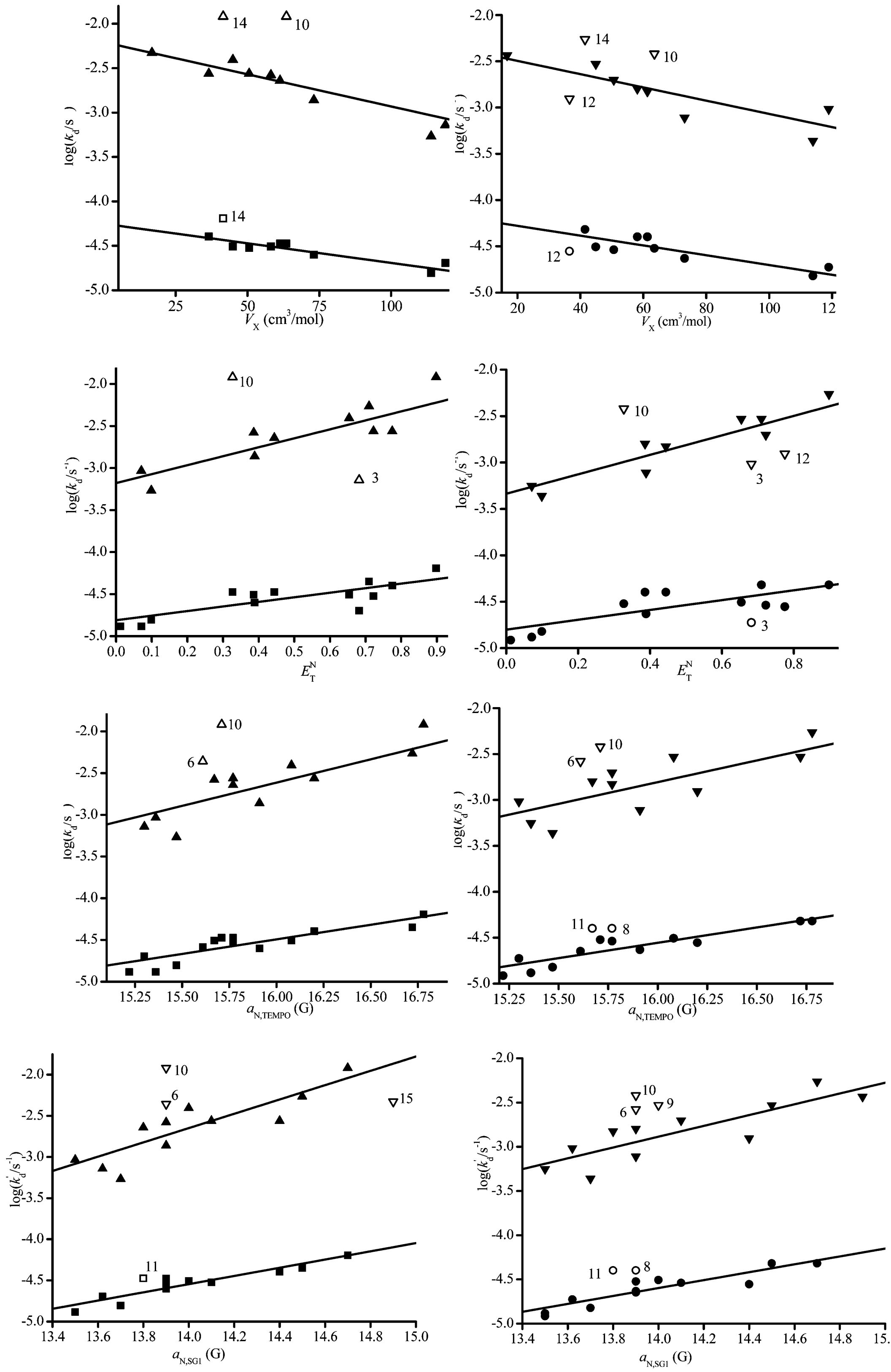


Figure 3. Linear correlation log(k_d'/s^{-1}) vs cybotactic parameters (from top to bottom: V_X, E_T^N, $a_{N,TEMPO}$, and $a_{N,SG1}$) for the minor (left) and the major (right) diastereoisomers of **1** (■, ●) and **2** (▲,▼) at 60 °C in various solvents. Open symbols denote outliers.

■ EXPERIMENTAL SECTION

Alkoxyamine **2** was prepared as previously reported.[5,7] k_d values were measured in 15 solvents using ^{31}P NMR with TEMPO as alkyl radical scavenger (2 equiv with respect to alkoxyamine) using the reported procedure as exemplified in Scheme 2.[5−7,33] A 0.1 mL portion of DMSO-d_6 as deuterated solvent with (MeO)$_3$PO as external reference (10 mM, ^{31}P NMR, δ = 0 ppm) were added to a probe filled with 0.6 mL of solution of alkoxyamine (40 mM) and TEMPO (2 equiv).

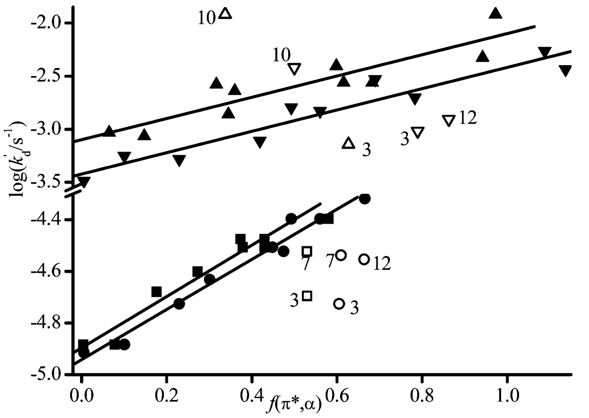


Figure 4. Plots of the KAT relationships for the minor (■, ▲) and the major (●, ▼) diastereoisomers of **1** (■, ●) and of **2** (▲, ▼). Open symbols denote outliers.

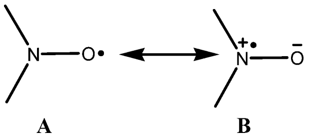


Figure 5. Mesomeric forms of the nitroxyl moiety.

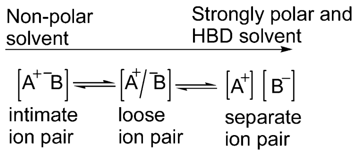


Figure 6. Different ion pairs depending on the solvent.

k_d values are given by eq 23, with C_0 being the initial concentration of alkoxyamine and t the time.[33] The activation energies E_a are given

$$\ln \frac{C}{C_0} = -k_d t \tag{23}$$

by eq 24, with the frequency factor $A = 2.4 \times 10^{14}$ s^{-1}, the temperature T, and the constant $R = 8.314$ J^{-1} K^{-1} mol^{-1}.[34]The configurations of

$$k_d = Ae^{-E_a/RT} \tag{24}$$

the minor and major diastereoisomers of **1** and **2** were ascribed to *RR*/*SS* and *RS*/*SR*, respectively, as given previously.[5]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table 1SI, gathering nitrogen hyperfine coupling constants $a_{\mathrm{N,TEMPO}}$ and $a_{\mathrm{N,SG1}}$, normalized Dimroth−Reichardt polarity parameter E_T^N, intrinsic volume of solvent V_X, refractive index n, molar volume V_M, relative permittivity ε_r, cohesive pressure c, Koppel−Palm basicity parameter B, hydrogen bond donor (HBD) parameter α, hydrogen bond acceptor (HBA) parameter β, polarity/polarizability parameter π^*, and discontinuous polarizability correction term δ, and Table 2SI, gathering the rate constants of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(30) Taking into account that the accepted error on E_a values is around ±1 kJ/mol. implying an error of 0.1 in log k_d'.

(31) The polarizability parameter is given by $(n^2 - 1)/2n^2 + 1)$ or $(n^2 - 1)/(n^2 + 2)$ on the basis of the refractive index n; the Kirkwood function is given by $(\varepsilon_r - 1)/(2\varepsilon_r + 1)$ or $(\varepsilon_r - 1)/(\varepsilon_r + 2)$, on the basis of the relative permittivity ε_r, the solvent basicity parameter B, the normalized Reichardt polarity solvent E_T^N, Hildebrand's solubility parameter δ, and the molar volume V_M of the solvent.

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