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# Long-range polar and steric effects in propionate-SG1-type alkoxyamines (SG1-CHMeCOOX): a multiparameter analysis†

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ABSTRACT: The effects of the substituent X on the homolysis rate constants ($k_d$) of SG1-propionate type alkoxyamines (SG1-CHMeCOOX) are analyzed by a multiparametric equation with $\upsilon$, the steric constant and $\sigma_I$, the polar inductive/field Hammett constant of X. An influence of long-range polar and steric effects on $k_d$ was observed, that is, decrease in $k_d$ with increasing size of the X group and increase in $k_d$ with increasing polarity of the X group. Copyright © 2006 John Wiley & Sons, Ltd.
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KEYWORDS: alkoxyamines; multiparameter analysis; long-range effects; polar and steric effects; homolysis

## INTRODUCTION

A decade ago, Rizzardo[1] and Georges[2] showed that it was possible to prepare well-defined living/controlled polymers using nitroxyl radicals as controllers. Nitroxide mediated polymerization (NMP) was born[3,4] and following this pioneering work, numerous studies have been carried out to elucidate the mechanism[5] and the kinetics of NMP processes,[6–8] to prepare new materials[3,9,10] and to develop efficient initiators/controllers.[11–16] Scheme 1 displays the ideal NMP process, with $k_d$ the rate constant for the homolysis of the C—ON bond of the alkoxyamine (so-called dormant species), $k_c$ the rate constant for the reformation of the alkoxyamine, $k_p$ the propagation rate constant of the polymerization and $k_t$ the self-termination rate constant of the reactions yielding dead polymers.

Alkoxyamines ($R_1R_2NOR_3$) are the key intermediates[5] of a NMP process and the strength of the C—ON bond is a crucial parameter to control.[6,11,15,16] It has been shown that the activation energy ($E_a$) of their homolysis is a good estimate of the value of the bond dissociation energy (BDE) of the C—ON bond.[17,18] We[15,17,19–22] and others[11,23–29] have shown that the C—ON bond of alkoxyamines was either strengthened by anomeric[26,29] (heteroatom bonded to the carbon) and polar[11,22,26,28,29] (electron withdrawing groups (EWG) bonded to the nitrogen atom) effects or weakened by the stabilization[11,17,21,23,24,26,29] of the released alkyl and nitroxyl[29] (intramolecular hydrogen bond IHB) radicals, and by the steric strain and polar effects of both alkyl and nitroxyl fragments.[11,13–29] Recently, Ananchenko et al.[30,31] observed a decrease in $k_d$ with bulkier alkyl groups. Thus, we investigated the influence of this long range steric effect and observed that the values of $k_d$ decreased linearly (Eqns 1(a) and 1(b)) with the increasing size of the substituent X of SG1-CHMeCOOX alkoxyamines **1–9** (Scheme 2).[32] Furthermore, it was noted that alkoxyamines **13** and **14** (SG1-CHMeCOOPh-4-Z type, Scheme 2) exhibited long-range polar effect, that is $k_d$ increased with the increasing electron-withdrawing capacities of the Z groups.[32] A thorough study of the series **10–17** showed a clear influence of the polarity of the benzene ring *para*-substituent on $k_d$ but the importance of the effect, that is the slope of the regression, was different for each isomer (Eqns 2(a) and 2(b)).[33] Such difference can be ascribed either to a different steric effect of the aromatic ring,[34,35] for each isomer or to a polar effect depending on the conformation[36–38] of the alkoxyamine, or even to stereoelectronic effects.[39] Aiming to discriminate between these three possibilities, in this work we prepared alkoxyamines **18–22** containing halogenoalkyl groups ($CH_2CH_{3-n}X_n$, X = F, Cl, and Br, Scheme 2). The homolysis rate constants $k_d$ of both isomers were measured

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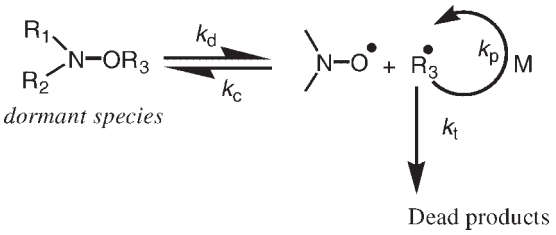
†In memoriam of Prof. Hanns Fischer, deceased 22 February 2005




**Scheme 1**

and correlated to the steric ($E_s$) and polar ($\sigma_I$) Hammet constants.

For *RR/SS* isomers:

$$\log\frac{k_d}{s^{-1}} = -3.07(\pm0.04) + 0.13(\pm0.02) \times E_s \quad (1a)$$

For *RS/SR* isomers:

$$\log\frac{k_d}{s^{-1}} = -2.59(\pm0.03) + 0.14(\pm0.02) \times E_s \quad (1b)$$

For *RR/SS* isomers:

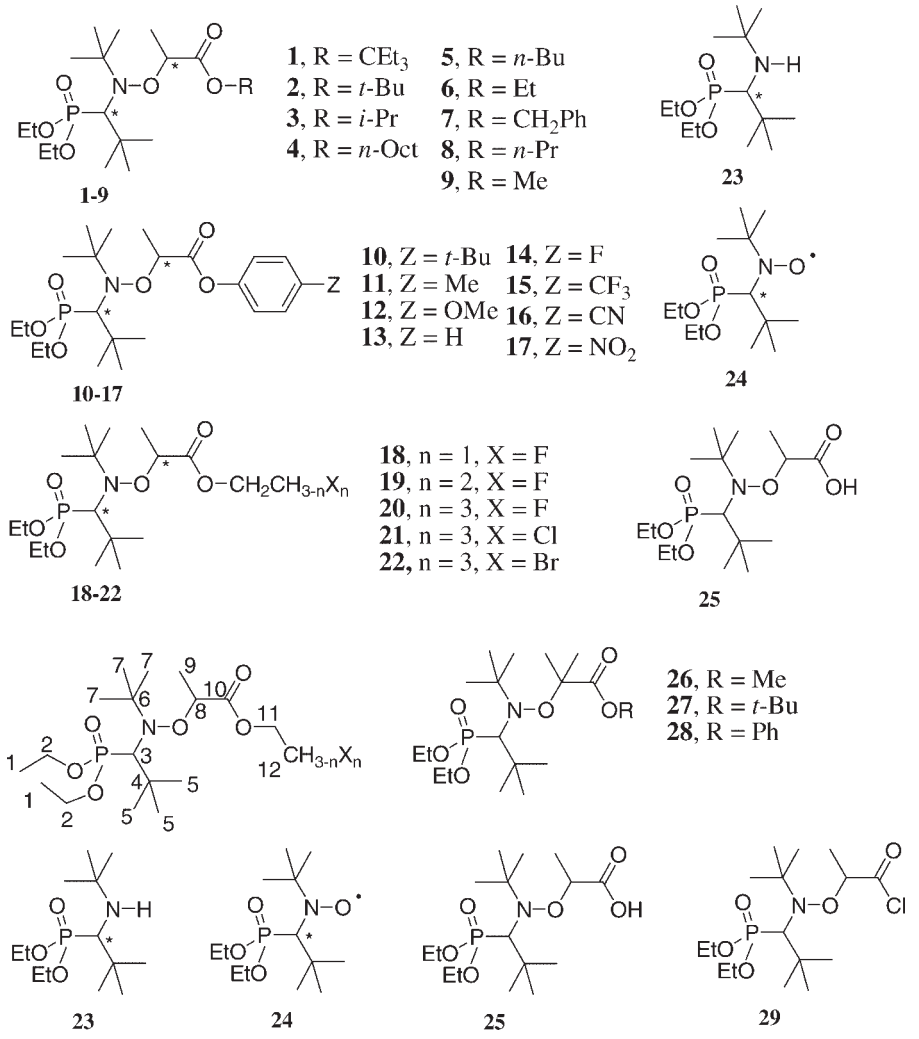
$$\log\frac{k_d}{s^{-1}} = -4.3(\pm0.1) + 4.3(\pm0.2) \times \sigma_{I,4-XC_6H_4} \quad (2a)$$

For *RS/SR* isomers:

$$\log\frac{k_d}{s^{-1}} = -3.6(\pm0.1) + 2.3(\pm0.3) \times \sigma_{I,4-XC_6H_4} \quad (2b)$$

## EXPERIMENTAL SECTION

Solvents for synthesis, triethylamine, 4-(dimethylamino)pyridine (DMAP), thionyl chloride ($SOCl_2$), and halogenoalcohols were purchased from Aldrich and used as received. TEMPO was purchased from Acros and sublimed. *tert*-Butylbenzene was purchased from Aldrich and purified by a conventional procedure.[40] Amine **23** was prepared as previously described[12] and used as internal standard for kinetic experiments. Nitroxyl radical **24** (SG1, Scheme 2) was kindly provided by Arkema and alkoxyamine **25** (Scheme 2) was prepared as already described.[32] Reactions were monitored by TLC (60 F 240 silica gel plates, eluent ethyl acetate/pentane 1/1), with UV and phosphomolybdic acid detection. Alkoxyamines were purified by chromatography (60 Silica gel, 70–230




**Scheme 2**

mesh, Merck), eluent: ethyl acetate/pentane 3/1. NMR experiments were performed in $CDCl_3$ on a 300 Avance Bruker spectrometer ($^1$H 300 MHz, $^{13}$C 75.48 MHz and $^{31}$P 121.59 MHz) in the Spectropôle (Marseille) where the elemental analyses were also performed. 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. The experimental procedure for kinetic measurements by $^{31}$P-NMR spectroscopy has been described earlier,[41] *tert*-butylbenzene was used as a solvent and a twofold excess of TEMPO was employed as radical trap.

### General procedure

A solution of **25** (4.0 g, 11.0 mmol) in $CH_2Cl_2$ was degassed by nitrogen bubbling for 10 min. Then, 3 equivalents $SOCl_2$ (2.4 mL, 33.0 mmol) were added under nitrogen atmosphere. The mixture was stirred for 45 min at room temperature and the excess of $SOCl_2$ was removed under vacuum (0.1 mb) to yield alkoxyamine **29**. Crude **29** was diluted in ether and then a 20 mL ether solution of alcohol (2 eq.), $Et_3N$ (1 eq., 1.5 mL, 11 mmol) and DMAP (0.4 eq., 0.3 g, 2.4 mmol) was added under nitrogen atmosphere. A white solid precipitated and the mixture was stirred for 4 h at room temperature. The white solid was filtered off and the solvent removed to yield oil. The oil was dissolved in 30 mL of ether, then washed three times with 15 mL of $NH_4Cl$ 5% aqueous solution, three times with 15 mL of a saturated sodium carbonate aqueous solution and with water to neutral pH. The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed to yield oil which was purified by column chromatography to afford alkoxyamines **18–22** (see SI).

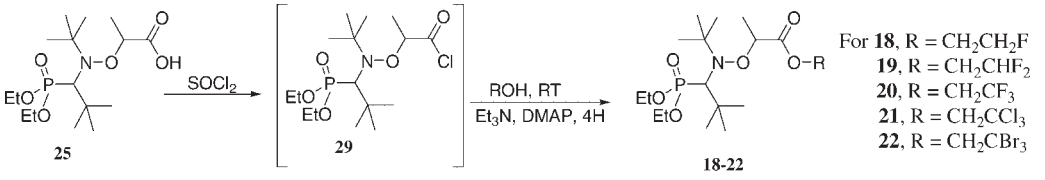
## RESULTS

Alkoxyamines **18–22** were prepared as depicted in Scheme 3.[32,33] Since each of these alkoxyamines exhibits two chiral centers (see Scheme 2), two isomers were obtained for each molecule. Their $^{31}$P NMR signals were not significantly different from those of series **1–17**. Therefore, with the absolute configurations attributed to **9** and **17**[42] given by the X-ray structures, the $^{31}$P NMR shifts of *ca.* 24.7 and 24.0 ppm correspond to the *RR/SS* and *RS/SR* diastereoisomers, respectively (See Experimental and Table 1).[32,33]

The $k_d$ of both diastereoisomers were measured in a single $^{31}$P NMR by monitoring the decay of the alkoxyamine, and given by Eqn (3).[41]

$$\ln \frac{[\text{alkoxyamine}]_t}{[\text{alkoxyamine}]_0} = -k_d \cdot t \qquad (3)$$

Activation energies $E_a$ were estimated using the average frequency factor $2.4 \times 10^{14}\ s^{-1}$ defined in the




**Scheme 3**

**Table 1.** $^{31}$P NMR shifts $\delta$, homolysis rate constants $k_d$, activation energies $E_a$ for alkoxyamines **18–22**

| | $\delta$ (ppm)[a] | | | $k_d$ ($10^{-4}$ s$^{-1}$)[c] | | $E_a$ (kJ/mol)[d] | | $k_d^{120}$ ($10^{-4}$ s$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|---|
| | *RR/SS* | *SR/RS* | $T$ (°C)[b] | *RR/SS* | *SR/RS* | *RR/SS* | *SR/RS* | *RR/SS* | *SR/RS* |
| **18** | 24.6 | 24.2 | 110 | 3.4 | 8.4 | 130.7 | 127.6 | 10.2 | 26.3 |
| | | | 111 | 4.2 | 13.0 | | | | |
| **19** | 24.4 | 24.2 | 110 | 6.1 | 12.6 | 128.9 | 126.7 | 17.7 | 34.6 |
| | | | 107 | 4.8 | 9.0 | | | | |
| **20** | 24.3 | 24.0 | 111 | 10.5 | 23.8 | 128.1 | 125.3 | 22.6 | 53.2 |
| | | | 109 | 6.2 | 16.1 | | | | |
| **21** | 24.9 | 24.6 | 109 | 5.3 | 13.3 | 129.1 | 126.4 | 16.6 | 38.0 |
| | | | 107 | 4.2 | 9.4 | | | | |
| **22** | 24.5 | 24.1 | 111 | 5.0 | 12.1 | 130.0 | 127.3 | 12.6 | 28.8 |
| | | | 109 | 3.9 | 9.0 | | | | |

[a] Amine **23** as internal standard in $C_6D_6$/*tert*-butylbenzene $\delta = 31.0$ ppm.
[b] Temperature $\pm$ 1°C.
[c] Errors were less than 5%.
[d] $E_a \pm 2$ kJ mol$^{-1}$.

literature,[17,29] and then all the $k_d$ were re-estimated at 120 °C to facilitate the comparison with published data. There are more than 40 Arrhenius parameters available in the literature, and most of them are in the region $5 \times 10^{13}\,s^{-1}$–$5 \times 10^{14}\,s^{-1}$.[43] Because of the $A$–$E_a$ compensation error effect,[44] it is very difficult to determine small changes in $A$ values; therefore, it is easier to use an averaged frequency factor to determine $E_a$ values, and then to estimate $k_d$ at the suitable temperature for comparison. Although all the $E_a$ values shown in Table 1 are within the experimental error ($\approx 2\,kJ\,mol^{-1}$), the values of $k_d$ are accurate enough (less than 10% error) for the discussion. Furthermore, for alkoxyamines **10**–**17**, it was shown that the plot $k_d$ versus $\sigma_I$ at 120 °C afforded similar regression coefficients than the plot at 110 °C, supporting the use of $A = 2.0 \times 10^{14}\,s^{-1}$ to estimate $k_d$ at temperature close to the experimental one.[33] The plot of $k_d$ versus ($\sigma_I$, $E_s$) for **1**–**9**, and **18**–**22** (not reported), at 110 °C, afforded close regression coefficients. Values of $k_d$, $^{31}P$ NMR shifts, temperatures, $k_d$ at 120 °C and $E_a$ values of **18**–**22** are gathered in Table 1. The polar[45] ($\sigma_I$) and steric[35] ($E_s$) constants of $CH_2CH_2F$, $CH_2CHF_2$, $CH_2CF_3$, $CH_2CCl_3$, and $CH_2CBr_3$ were estimated with Eqns (4)[46] and (5),[35] respectively. They are stored in Table 1SI along with the Charton[47,48] ($\upsilon$) steric constants, and the missing $\upsilon$ for $CH_2CH_2F$, $CH_2CHF_2$, $CH_2CF_3$, $CH_2CCl_3$, and $CH_2CBr_3$ groups are given by Eqn (6).[49]

$$\sigma_I(CH_2R) = 0.416 \times \sigma_I(R) - 0.0103 \tag{4}$$

$$E_s(CR_1R_2R_3) = -2.104 + 3.429 \times E_s(R_1) + 1.978 \times E_s(R_2) + 0.649 \times E_s(R_3) \tag{5}$$

$$\upsilon = 0.502 - 0.477 \times E_s \tag{6}$$

Fujita et al.[35] showed that the steric effect can be represented by a linear combination (Eqn (5)) of the individual Taft steric constants for a group R, noted $E_s(R_i)$, with $i$ being the rank related to the value of $E_s(R_i)$, that is its size (the more negative $E_s(R_i)$ is, the larger $R_i$ is).

$E_a$ values of alkoxyamines **1**–**17** were determined in our previous works.[32,33] $E_a$ values, Taft ($E_s$) and Charton ($\upsilon$) steric constants, polar ($\sigma_I$ and $\sigma_{I,Ph\text{-}4\text{-}Z}$) Hammett constants, steric ($\upsilon_{CHMeCOOX}$) and polar ($\sigma_{I,CHMeCOOX}$) constants of the CHMeCOOX groups in alkoxyamines **1**–**22** are listed in Table 1SI. In a recent paper,[21] we provided an analysis of the $k_d$ values in terms of stabilizing ($\sigma_{RS}$), polar ($\sigma_I$) and steric ($\upsilon$) effects (Eqn (7)). It is generally accepted that the size and the polarity of the alkoxy group of the ester function exert only a weak influence – if any – onto the reactive center.[50] Despite the presence of long-range (4–7 σ bonds) polar and steric effects, it would be interesting to correlate series **1**–**22** to Eqn (7). It was assumed that the halogenoalkyl groups exhibited the same steric effect for both diastereoisomers and that the polar effect was dependent only on the position of the COOR group and not on the position of the $CH_2CH_{3-n}X_n$ groups. To avoid using too many parameters, and because the $E_s$ and $\upsilon$ values are highly correlated (Eqn (6)),[49] the $\upsilon$ values were used to define the new set of steric constants. Thus, new constants $\upsilon_{CHMeCOOX}$ and $\sigma_{I,CHMeCOOX}$ have to be developed to account for the steric and polar influence of the X groups of the ester moiety (Eqns (8) and (9)) with $\xi$ and $\kappa$ the correction terms for the steric and polar effects of the X group, respectively.

$$\log k_d = -14.3(\pm 1.3) + 15.3(\pm 2.2) \times \sigma_{RS} + 19.5(\pm 3.0) \times \sigma_I + 7.0(\pm 1.1) \times \upsilon \tag{7}$$

$$R^2 = 0.85 \qquad N = 19 \qquad s = 0.80 \qquad F_{99,99} = 29$$

Assuming that Eqn (7) holds for the series **1**–**22** and that the stabilizing effect is not affected by the ester substituent,[33] and using alkoxyamines **2** and **9** (same polar effect) with $\upsilon_{CHMeCOOMe}$ (1.0) and $\sigma_{I,CHMeCOOMe}$ (0.09) as references, the values of −0.103 and −0.095 for $\xi$ of *RR/SS* and *RS/SR* diastereoisomers, respectively, were estimated with Eqns 10–14. Because the slopes of log ($k_d$) versus $\sigma_I$ for the two isomers are too different from one another (Eqns 2(a) and 2(b)) and because the values of $E_s$ and $\upsilon$ for the phenyl group are not clearly established,[34,35,47,49] the series **10**–**17** was not used to determine the values of $\kappa$. The values of 0.283 and 0.251 for $\kappa$ of *RR/SS* and *RS/SR* diastereoisomers, respectively, were estimated with Eqns (15)–(18), when applied to alkoxyamines **9** and **20**. For the sake of simplicity, averaged values of −0.099 and 0.267 were used for $\xi$ and $\kappa$, respectively.

$$\upsilon_{CHMeCOOX} = \upsilon_{CHMeCOOMe} + \xi \times \upsilon_X - \xi \times \upsilon_{Me} \tag{8}$$

$$\sigma_{I,CHMeCOOX} = \sigma_{I,CHMeCOOMe} + \kappa \times \sigma_{I,X} - \kappa \times \sigma_{I,Me} \tag{9}$$

$$\log k_{d,\mathbf{9}} = \log k_0 + \rho_{RS} \times \sigma_{RS,CHMeCOOMe} + \rho_I \times \sigma_{I,CHMeCOOMe} + \delta \times \upsilon_{CHMeCOOMe} \tag{10}$$

$$\log k_{d,\mathbf{2}} = \log k_0 + \rho_{RS} \times \sigma_{RS,CHMeCOO\mathit{t}\text{-}Bu} + \rho_I \times \sigma_{I,CHMeCOO\mathit{t}\text{-}Bu} + \delta \times \upsilon_{CHMeCOO\mathit{t}\text{-}Bu} \tag{11}$$

$$\frac{\Delta \log k_d}{\delta} = \upsilon_{CHMeCOOMe} - \upsilon_{CHMeCOO\mathit{t}\text{-}Bu} \tag{12}$$

$$\upsilon_{CHMeCOO\mathit{t}\text{-}Bu} = \upsilon_{CHMeCOOMe} + \xi \times \upsilon_{\mathit{t}\text{-}Bu} - \xi \times \upsilon_{Me} \tag{13}$$

$$\xi = \frac{\Delta \log k_d}{\delta(\upsilon_{Me} - \upsilon_{\mathit{t}\text{-}Bu})} \tag{14}$$

$$\log k_{d,\mathbf{20}} = \log k_0 + \rho_{RS} \times \sigma_{RS,CHMeCOOCH_2CF_3} + \rho_I \times \sigma_{I,CHMeCOOCH_2CF_3} + \delta \times \upsilon_{CHMeCOOCH_2CF_3} \quad (15)$$

$$\frac{\Delta \log k_d - \delta\xi(\upsilon_{Me} - \upsilon_{CH_2CF_3})}{\rho_I} = \sigma_{I,CHMeCOOMe} - \sigma_{I,CHMeCOOCH_2CF_3} \quad (16)$$

$$\sigma_{I,CHCOOCH_2CF_3} = \sigma_{I,CHCOOMe} + \kappa \times \sigma_{I,CH_2CF_3} - \kappa \times \sigma_{Me} \quad (17)$$

$$\kappa = \frac{\Delta \log k_d - \delta\xi(\upsilon_{Me} - \upsilon_{CH_2CF_3})}{\rho_I(\sigma_{Me} - \sigma_{I,CH_2CF_3})} \quad (18)$$

Because the phenyl ring is a steric "*Janus*" group,[34,35] the value of $E_s$ ($E_s = -1.8$, Table 1SI) was chosen to yield the best fit (Eqns 23(a) and 23(b), Table 2).

## DISCUSSION

When the $k_d$ of **18–22** are compared to those of **9** (Table 1SI), the importance of the polar effect is not striking, that is **20** decomposes roughly two times faster than **9**. On the other hand, assuming the absence of any polar effect, Eqns 1(a) and 1(b) give 6.8, 5.9, 5.1, 4.3, and $4.0 \times 10^{-4}\,s^{-1}$, and 20.3, 17.5, 14.8, 12.2, and $11.3 \times 10^{-4}\,s^{-1}$ as values of $k_d$ for *RR/SS* and *RS/SR* isomers of alkoxyamines **18–22**, respectively. Keeping in mind that the distance between the halogen atom(s) and the reactive center is 5 σ-bonds, the comparison of these estimated values with the experimental values (Table 1SI) shows that the polar effect increases from weak in **18** ($k_d$ measured *ca.* 1.5 times as high as $k_d$ estimated) to strong in **20** ($k_d$ measured *ca.* 4.5 times as high as $k_d$ estimated). This increase is even more striking (8 and 4 times stronger) when the estimated $k_d$ of the isomers of **17** (5.0 and $14.0 \times 10^{-4}\,s^{-1}$) was compared with the experimental $k_d$ values (38.0 and $56.4 \times 10^{-4}\,s^{-1}$). Thus, the values of $k_d$ were analyzed as a linear combination of the long-range polar and steric effects (Eqn (19)).

$$\log(k_d/s^{-1}) = \log k_0 + \rho_I \times \sigma_I + \delta \times E_s(\text{or } \delta' \times \upsilon) \quad (19)$$

As expected, the plots log ($k_d/s^{-1}$) versus $\sigma_I$ (not shown, Eqns 20(a) and 20(b) in Table 2) and log ($k_d/s^{-1}$) versus $E_s$ (Fig. 1, Eqns 21(a) and 21(b) in Table 2) display scattered dots for the alkoxyamines of series **1–9** and **18–22**. On the other hand, a biparameter ($E_s$, $\sigma_I$) correlation exhibits good statistical output (Eqns 22(a) and 22(b), Table 2) and accounts for the influence of the sizes and the polarities of the ester groups for **1–9** and **18–22** (Fig. 2). The coefficients $\rho_I$ obtained in Eqns 22(a) and 22(b) are different for each isomer and different from those in Eqns 2(a) and 2(b) while coefficients $\delta$ are the same in Eqns 1(a) and 1(b), and Eqns 22(a) and 22(b). The close values of $\Delta\rho_I$ for the series **1–9** and **18–22** ($\Delta\rho_U = 0.82$) and for the series **10–17** ($\Delta\rho_U = 1.0$) leads to discard the possibly enhanced polar effect due to the

**Table 2.** Coefficients $\rho_I$, $\delta$, and $\delta'$ for the linear combinations of $k_d$ (Eqn (19)) at 120°C with the molecular descriptors for the polar ($\sigma_I$) and the steric ($E_s$ or $\upsilon$) effects for both isomers (a for *RR/SS* and b for *RS/SR*) of series **1–22**, and the statistical outputs

| Equations | log $k_{d,0}$ | $\rho_I$[a] | $\delta$[b] | $\delta'$[c] | n[d] | $s$[e] | $R^{2}$[f] | $t$[g] | $F$[h] |
|---|---|---|---|---|---|---|---|---|---|
| 20a | −3.20 (±0.06) | 2.98 (±0.72) | — | — | 14 | 0.18 | 0.59 | 99.87 | — |
| 21a | −2.96 (±0.11) | — | 0.08 (±0.06) | — | 14 | 0.26 | 0.54 | 81.25 | — |
| 22a | −3.04 (±0.04) | 3.53 (±0.34) | 0.13 (±0.02) | — | 14 | 0.09 | 0.92 | 99.99 | 61 |
| 23a | −3.04 (±0.03) | 3.66 (±0.19) | 0.13 (±0.02) | — | 22 | 0.07 | 0.95 | 99.99 | 191 |
| 24a | −2.99 (±0.17) | — | — | −0.08 (±0.14) | 14 | 0.28 | 0.02 | 40.00 | |
| 25a | −2.93 (±0.06) | 4.02 (±0.44) | — | −0.31 (±0.06) | 14 | 0.10 | 0.89 | 99.99 | 43 |
| 26a | −2.93 (±0.05) | 4.05 (±0.24) | — | −0.31 (±0.04) | 22 | 0.08 | 0.94 | 99.99 | 147 |
| 20b | −2.73 (±0.06) | 2.16 (±0.71) | — | — | 14 | 0.18 | 0.44 | 99.00 | — |
| 21b | −2.50 (±0.09) | — | 0.10 (±0.05) | — | 14 | 0.21 | 0.26 | 94.00 | — |
| 22b | −2.57 (±0.03) | 2.71 (±0.30) | 0.13 (±0.02) | — | 14 | 0.07 | 0.91 | 99.99 | 59 |
| 23b | −2.56 (±0.03) | 2.61 (±0.16) | 0.13 (±0.01) | — | 22 | 0.06 | 0.94 | 99.99 | 140 |
| 24b | −2.50 (±0.14) | — | — | −0.13 (±0.12) | 14 | 0.23 | 0.10 | 81.00 | |
| 25b | −2.44 (±0.05) | 3.23 (±0.38) | — | −0.31 (±0.05) | 14 | 0.09 | 0.88 | 99.99 | 41 |
| 26b | −2.45 (±0.05) | 2.98 (±0.23) | — | −0.29 (±0.04) | 22 | 0.08 | 0.90 | 99.99 | 87 |

[a] Coefficient for the polar effect $\sigma_I$.
[b] Coefficient for the steric effect $E_s$.
[c] Coefficient for the steric effect $\upsilon$.
[d] Number of data.
[e] Standard deviation.
[f] Square of the linear regression coefficient.
[g] Student *t*-test given in per cent.
[h] *F*-test at 99.99% confidence.

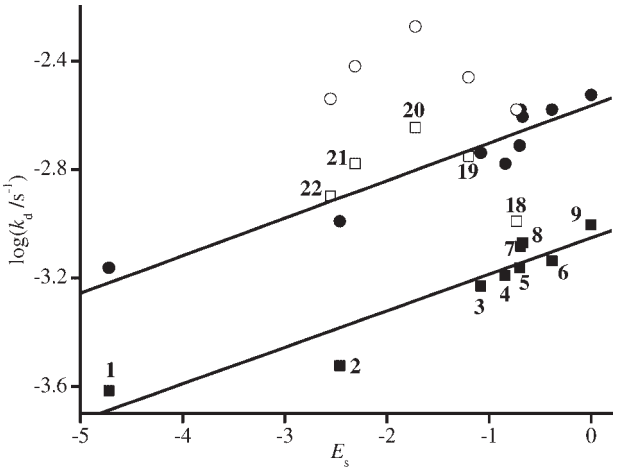



**Figure 1.** Plot of log ($k_d/s^{-1}$) at 120 °C versus $E_s$ for alkoxyamines **1–9** (filled symbols) and **18–22** (open symbols). (■, □) *RR/SS* isomers, (●, ○) *RS/SR* isomers. The straight lines are for Eqns 1(a) and 1(b) and for data **1–9**

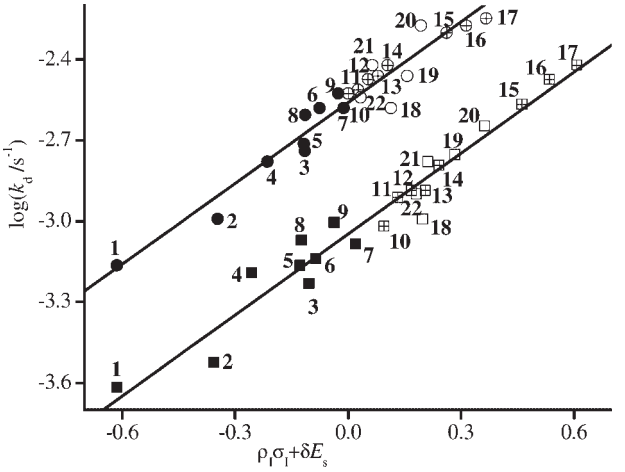



**Figure 2.** Plot of log ($k_d/s^{-1}$) at 120 °C versus Eqns 23(a) (square) and 23(b) (circle), (■, □, ⊞) RR/SS isomers, (●, ○ ⊕) RS/SR isomers, for alkoxyamines **1–9** (filled symbols), **10–17** (crossed symbols), and **18–22** (open symbols)

position of the aromatic ring.[36–38] When all the alkoxyamines **1–22** are taken into account, biparameter Eqns 23(a) and 23(b) well account for the polar and steric effects of the ester group. The weaker polar effect for the *RS/SR* than for the *RR/SS* isomer is due to the dependence of $\sigma_I$ on the geometry of the molecule (the anchimeric effect, see Ref. [42]). It is noteworthy that the long-range steric effect does not depend on the configuration of the alkoxyamine, that is both isomers exhibit the same slope (Eqns (1) and (21)–(26) in Table 2). With weighting equations,[51] it appears that the polar effect is the major contribution (54%–70%, Table 2SI) to the cleavage. The steric contribution is larger in Eqn (22) than in Eqn (23) (Table 2SI). In fact, for Eqn (22), 9 alkoxyamines (series **1–9**) exhibit a pure steric effect and 5 alkoxyamines (series **18–22**) exhibit steric and polar effects, whereas for Eqn (23), the number of molecules (9 alkoxyamines) exhibiting a pure steric effect is balanced by the number of molecules (8 alkoxyamines, series **10–17**) exhibiting a pure polar effect. All the comments made on and from the correlations using $E_s$ as steric molecular descriptors hold for the correlations using $\upsilon$ but the statistical output are slightly poorer (Eqns (24)–(26a and b), Table 2).

Because the statistical output and weight coefficients (Table 2SI) of Eqn (28) (three parameters) are very close to those of Eqn (27) (five parameters), there is no need to use more than three parameters to fit the whole set of data. When the two isomers of each of the alkoxyamines **1–22** are fitted with Eqn (28) (Fig. 2SI), the *RR/SS* isomer data are closer to the straight line than the *RS/SR* isomer data. This result could mean that the *RR/SS* and the *RS/SR* isomers exhibit a *normal* and an *enhanced* polar effect, respectively. The *enhanced* polar effect could be due to the *RS/SR* configuration which allows either a preferred conformation, in which the distance and the angle between the reactive center and the polar group are optimum, or a possible interaction between the ester group and the phosphoryl group.[42]

$$\log\frac{k_d}{s^{-1}} = -14.62(\pm0.74) + 15.75(\pm1.25)\times\sigma_{RS} + 19.75(\pm1.65)\times\sigma'_I + 7.28(\pm0.61)\times\upsilon' + 3.49(\pm0.91)\times\sigma_I - 0.27(\pm0.12)\times\upsilon \quad (27)$$

$$R^2 = 0.85 \qquad s = 0.42 \qquad N = 61 \qquad F_{99,99} = 65$$

$$\log\frac{k_d}{s^{-1}} = -14.03(\pm0.73) + 15.38(\pm1.30)\times\sigma_{RS} + 18.83(\pm1.45)\times\sigma'_I + 6.79(\pm0.60)\times\upsilon' \quad (28)$$

$$R^2 = 0.84 \qquad s = 0.44 \qquad N = 61 \qquad F_{99,99} = 97$$

We have already discussed the short- and long-range polar effect,[20,21,33] and ascribed it to the change in electronegativity difference between the oxygen and the carbon atoms of the C—ON bond. This involves stabilization or destabilization (small $\Delta\chi$) of the alkoxyamine, that is decrease or increase of $k_d$, respectively. However, the presence of a long-range effect is better accounted for by through-space transmission (field effect) of the substituent polarity to the reactive center rather than by through σ-bond transmission (inductive effect) of this polarity to the reactive center.[36,42,52] Such through-space transmission of the polarity may account for the $k_d$ increase with the increasing length of the polybutylacrylate-SG1 polymer, as observed by the authors.[53] That is, assuming a folded polymer chain, the longer the chain, the more numerous

the polar units close to the reactive center and therefore the higher the polarity at the carbon atom of the cleaved C—ON bond, the larger the values of $k_d$.

In a recent work,[30] we showed that the $k_d$s of TEMPO-based alkoxyamines did not exhibit such dependence on the size of the alkyl ester group. This absence of dependence could be due either to a very fast exchange process or to the alkyl fragment pre-set in the right conformation for the one-step homolysis pathway.

## CONCLUSION

Our results support and exemplify the presence of long-range steric and polar effects in ester SG1-based alkoxyamines **1**–**22**. The long-range steric effect is accounted for either by the presence of a conformer or by an activation entropy effect ($\Delta S^{\neq}$). The long-range polar effect is configuration dependent and thus resembles the field effect which depends on the proximity of the reaction center to the polar group. This long-range polar effect occurs in the initial state and was ascribed previously to the change in electronegativity difference between the atoms forming the cleaved bond.

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