Macromolecules **1998,** *31,* 9103−9105 **9103**

Decomposition Kinetics, Arrhenius Parameters, and Bond Dissociation Energies for Alkoxyamines of Relevance in "Living" Free Radical Polymerization

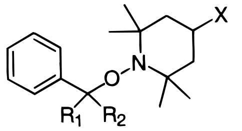
W. G. Skene,[†] S. T. Belt,[‡] T. J. Connolly,[†] Peter Hahn,[†] and J. C. Scaiano*,[†]

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5, and Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon PL4 8AA, U.K.

Received August 3, 1998
Revised Manuscript Received October 1, 1998

In the 1980s Rizzardo and co-workers established that vinyl free radical polymerization could be controlled by reversible capping with nitroxides, reflecting the weak C−O bond formed in the capping reaction.[1] The 1993 report by Georges et al.[2] discussing the preparation of low-polydispersity polystyrene by "living free radical polymerization" (LFRP) regulated by nitroxides has stimulated a widespread research effort in this area. The currently accepted mechanism is shown in Scheme 1. The key step is the reversible capping of the polymer chain by the nitroxide. This cap dissociates at temperatures around 125 °C to allow polymer growth.

A number of initiators mimicking the chain end (i.e. **I**−**IV**) have been reported by us and by others.[3−6] It is reasonable to assume that the C−O bond dissociation energy at the capped polymer end will be similar to those in other benzylic systems such as **I**−**IV**. A number of estimates of this bond dissociation energy (*D*) have been reported for these and related structures, ranging from 19 to 36 kcal/mol,[7−18] although the more recent determinations are in the 25−30 kcal/mol range, with the more highly substituted benzylic carbons corresponding to the lower bond energies, as expected.



I: $R_1 = R_2 = X = H$
II: $R_1 = X = H; R_2 = CH_3$
III: $R_1 = R_2 = CH_3; X = H$
IV: $R_1 = R_2 = H; X = OH$

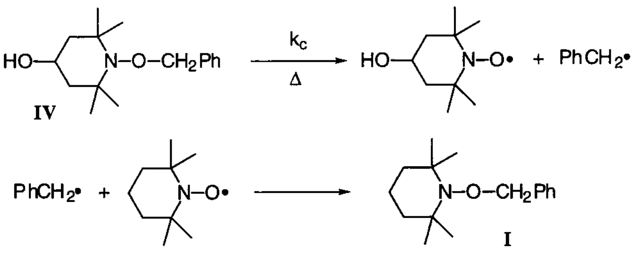
Much of the earlier experimental work on bond energies was performed under conditions of reversible C−O cleavage or where the activation energies for the back reaction have not been taken into consideration. While reversibility can be taken into account, it does lead to significantly more complex kinetic analysis (vide infra).

Compound **II** is probably be the best model compound for the actual polymer, since the nitroxide link involves a secondary benzylic site. The kinetics of the cleavage reaction are important not only in order to determine bond dissociation energies but also because they control the steady-state concentration of nitroxide and thus the overall polymerization kinetics. Further, to mimic a living process and obtain low polydispersities, it is necessary for the initiator decomposition to occur in a relatively short time compared with the overall polymerization process; this, in turn, requires knowledge of the initiator fragmentation kinetics. While several reports have either measured or estimated some of these kinetic parameters, this is the first systematic study of bond dissociation energies and kinetic parameters for a complete (primary, secondary, and tertiary) series. Further, our work has been performed under irreversible conditions for the cleavage reaction; much of the earlier work either has not taken into account reversibility or has led to considerably more complex data fittings, since under reversible conditions nitroxide buildup follows a $t^{1/3}$ rate law (t = time), from which kinetic parameters can be derived.[19]

Scheme 1

$$\text{Initiator} \longrightarrow 2\ R^\bullet$$
$$R^\bullet + C_6H_5CH{=}CH_2 \longrightarrow RSt_1^\bullet$$
$$RSt_n^\bullet + C_6H_5CH{=}CH_2 \longrightarrow RSt_{n+1}^\bullet$$
$$RSt_n^\bullet + \text{TEMPO} \underset{\substack{\text{reversible}\\ \text{capping}}}{\rightleftarrows} RSt_n\text{–TEMPO}$$

Scheme 2



IV

I

To facilitate the study of the kinetics of thermal cleavage of **I**−**IV**, it is important to make this process irreversible. This can be readily achieved by decomposing **I**−**IV** in the presence of a large excess of another nitroxide, as indicated in Scheme 2 for the example of **IV** (a similar approach has been reported).[5] Our choice of trapping nitroxide was 4-hydroxy-TEMPO for **I**−**III** and TEMPO for **IV**. This trap was used in ~7 times excess with respect of the alkoxyamine. At low conversions, the final concentration of nitroxide used as a trap was about 20−50 times larger than that of the nitroxide released as a product.[20] Note that in the absence of an efficient added scavenger most of the cleavage is masked by the rapid back reaction,[21,22] in a process that may lead to the apparent photostability of these materials, as expected from the Fischer−Ingold persistent radical effect.[23] Analysis for either product (by HPLC)[24] of the reaction (for example **IV** or TEMPO in the case of **I**) after different reaction times yields k_c. A small correction (<3%) to account for traces of disproportionation (giving the alkene and hydroxylamine) was introduced for **II** and **III**. The reactions were studied in the temperature ranges indicated in Table 1 in cyclohexanol as solvent. This proved to be a useful solvent allowing for a convenient temperature range; cleavage kinetics for other initiators show a modest solvent dependence.[5] These ranges are determined by the need to have experimental kinetics in a convenient time scale. The

---

* To whom address correspondence should be addressed. Phone: 613-562-5896. Fax: 613-562-5633. E-mail: tito@photo.chem.uottawa.ca.

[†] University of Ottawa.

[‡] University of Plymouth.

10.1021/ma9812229 CCC: $15.00

Table 1. Kinetic and Thermodynamic Data for the Decomposition of Alkoxyamines I−IV

substitution	E_a (kcal/mol)	log *A* (s^{-1})	*T* range (K)	τ^a (s) at 398 K	E_a (kcal/mol) back for reaction	BDE (*D*) (kcal/mol)
I; $R_1 = R_2 = X = H$	32.6[b]	13.6[c]	366−427	16100	1.8[d]	30.8
II; $R_1 = CH_3$; $R_2 = X = H$	30.7[e]	13.7[f]	348−393	1150	2.3[g]	28.4
III; $R_1 = R_2 = CH_3$; $X = H$	27.2[h]	14.0	308−348	6.8	2.6[g]	24.6
IV; $R_1 = R_2 = H$; $X = OH$	33.2	13.6	363−428	34500	1.8[d]	31.4

[a] Lifetime in seconds calculated as $1/k_c$. [b] Another value has been reported (23.4).[13] [c] Another value has been reported (11.9).[13] [d] Value derived from the literature[21,27] for a comparable solvent viscosity. [e] Other values have been reported (24.2 and 28.4,[14] 29.7,[16] 31.1,[7,10,18] 29.7 and 36.7,[17] and 19 and 27).[15] [f] Other values have been reported (13.5,[16] 13.3, and 14.8).[17] [g] Taken from the literature.[22] [h] A value of ~25 kcal/mol has also been determined.[28]

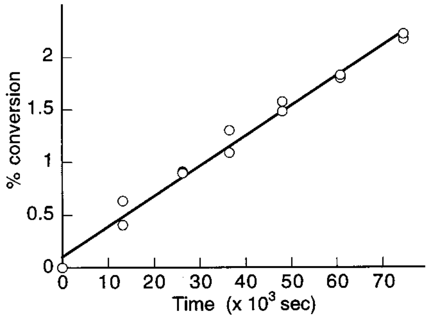


Figure 1. Determination of the rate constant for the formation of **I** from thermolysis of **IV** at 90 °C. Each point in Figure 2 is based on a plot of this type.

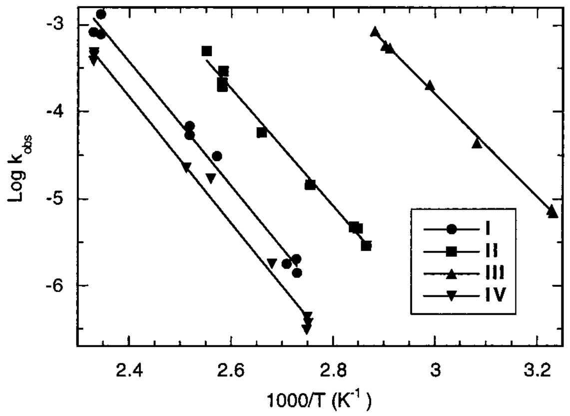


Figure 2. Arrhenius plots for the decomposition of **I**−**IV**. The corresponding Arrhenius data are presented in Table 1.

individual rate constants are obtained from plots of product formation as a function of time, as illustrated for the case of **IV** in Figure 1. The conversions were sufficiently low that a linear approximation (as shown in Figure 1) is adequate. These slopes are then plotted in an Arrhenius format (Figure 2) to yield a preexponential factor and an activation energy, as given in Table 1.

The activation energy determined from plots as illustrated in Figure 2 would correspond to *D* if the activation energy for the back reaction was zero; in fact these values are quite small and can be estimated on the basis of work by Ingold and co-workers;[21,22] the value was 1.8 kcal/mol for **IV**, thus leading to $D = 31.3 \pm 0.8$ kcal/mol. Table 1 summarizes the *D* values obtained in this manner. Preexponential factors are of the magnitude anticipated for a bond fragmentation with the corresponding entropic gain. It is unclear if the trend in preexponential factors in the **I**−**III** series (see Table 1) is real or within experimental error. If real, it may reflect a lower entropy of activation for **III** due to a more constrained ground-state geometry (i.e. a ground-state, rather than transition-state, effect).

The values in Table 1 are consistent with reported synthetic yields. Compounds **I**−**IV** can be prepared in high yields photochemically by photodecomposition of di-*tert*-butyl peroxide in the presence of TEMPO using the appropriate hydrocarbon (toluene, ethylbenzene, or cumene) as a solvent.[3] In contrast, thermal synthesis, where the activation energy for di-*tert*-butyl peroxide decomposition is 38.3 kcal/mol,[25] works well for toluene, gives a modest yield (42%) for ethylbenzene, and fails for cumene.[26] The decomposition of **I**−**IV** may be partially reversible (except for a minor fraction of disproportionation for **II** and **III**), since cross reactions are always favored in these systems,[23] thus increasing the tolerance for some cleavage. However, the synthetic failure for **III** can be attributed to an activation energy for decomposition far below that for the peroxide, thus suggesting that *D* for **III** is <38 kcal/mol, consistent with the expectation that this activation energy will be lower than that for **I** or **IV** (i.e., <32 kcal/mol).

Full control of LFRP as indicated in Scheme 1 will require the ability to control the dissociation of the nitroxide cap. Such control may be achieved by "tuning" the values of *D* or conceivably by utilization of photoinduced cap dissociation at lower temperatures.

Acknowledgment. This work has been supported by the Natural Sciences and Engineering Research Council of Canada. S.T.B. thanks the Royal Society for Chemistry for a J.W.T. Jones travel fellowship. Thanks are due to Drs. K. U. Ingold and H. Fischer for valuable discussions.

References and Notes

(1) Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1979**, *1*, 529. Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165. Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909. Moad, G.; Rizzardo, E.; Solomon, D. H. *Polym. Bull.* **1982**, *6*, 589. Beckwith, A. L. J.; Bowry, V. W.; O'Leary, M.; Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1003.

(2) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.

(3) Connolly, T. J.; Baldovi, M. V.; Mohtat, N.; Scaiano, J. C. *Tetrahedron Lett.* **1996**, *37*, 4919.

(4) Baldovi, M. V.; Mohtat, N.; Scaiano, J. C. *Macromolecules* **1996**, *29*, 5497.

(5) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722.

(6) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.

(7) Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391.

(8) Kazmaier, P. M.; Moffat, K. M.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. *Macromolecules* **1995**, *28*, 1841.

(9) Puts, R. D.; Sogah, D. Y. *Macromolecules* **1996**, *29*, 3323.

(10) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 2746.

(11) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. *Macromolecules* **1995**, *28*, 8453.

(12) Engel, P. S.; Duan, S.; Arhancet, G. B. *J. Org. Chem.* **1997**, *62*, 3537.

(13) Stipa, P.; Greci, L.; Carloni, P.; Damiani, E. *Polym. Degrad. Stab.* **1997**, *55*, 323.

(14) Li, I.; Howell, B. A. *Macromolecules* **1995**, *28*, 6692.

(15) Veregin, R. P. N.; Kazmaier, P. M.; Odell, P. G.; Georges, M. K. *Chem. Lett.* **1997**, *5*, 467.
(16) Goto, A.; Rerauchi, T.; Fukuda, T.; Miyamoto, T. *Macromolecules* **1997**, *18*, 3373.
(17) Fukuda, T.; Tsujii, Y.; Miyamoto, T. *Polym. Prepr.* **1997**, *38*, 723.
(18) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 4161.
(19) Fischer, H. *Macromolecules* **1997**, *30*, 5666.
(20) Typical initial concentrations are 20 mM for the alkoxyamine and 60 mM for the nitroxide trap.
(21) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4983.
(22) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1992**, *114*, 4992.
(23) Fischer, H. *J. Am. Chem. Soc.* **1986**, *108*, 3925.
(24) HPLC analyses were carried out using a Zorbax SB-C18 reverse-phase column with 85:15 methanol/water as eluent. The flow rate was 0.5 mL/min for the first 12 min and 1.5 mL/min after that. Results are based on products formed rather than comsumption of starting material, since at the low conversions used the latter is subject to considerable errors. Product concentrations (coupling and traces of disproportionation) were determined against authentic samples.
(25) Batt, L.; Christie, K.; Milne, R. T.; Summers, A. *Int. J. Chem. Kinet.* **1974**, *6*, 877.
(26) Hawker, C. J.; Barclay, G. G.; Orellana, A.; Dao, J.; Devonport, W. *Macromolecules* **1996**, *29*, 5245.
(27) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629.
(28) Kothe, T.; Marque, S.; Martschke, R.; Popov, M.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1553.

MA9812229