Quantum Mechanical Investigation on Bimolecular Hydrogen Abstractions in Butyl Acrylate-Based Free Radical Polymerization Processes

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INTRODUCTION

Acrylates are among the most important classes of vinyl monomers. Therefore, many studies have been dedicated to the investigation of the propagation and termination kinetics of acrylic compounds, facilitated by the development of modern techniques for reaction rate coefficient estimation based on pulsed-laser polymerization (PLP).[1,2] However, these studies have also revealed the importance of several side reactions that occur in parallel during the free-radical polymerization (FRP) of acrylic monomers which have consequences on the polymerization process and final polymer features. Prevalent among these side reactions are the hydrogen abstraction reactions, which are responsible for radical shifts from chain-end to more stabilized intrachain positions, thus modifying the average radical reactivity.

The impact of these secondary reactions was first observed during PLP combined with size exclusion chromatography (PLP-SEC) experiments, in which the measurement of the propagation rate coefficient (k_p) at high temperature (i.e., over 60 °C) can be corrupted by the presence of intramolecular chain transfer reactions.[3−5] This peculiar hydrogen abstraction also referred to as backbiting leads to the formation of midchain radicals (MCRs),[6,7] which usually propagate at a lower rate than the chain-end radical (CER) and lead to the formation of branches. Backbiting kinetics for relevant acrylate systems has been widely investigated in recent decades, and their connection with the formation of short-chain branches has been established. Backbiting is particularly favored among the hydrogen abstraction reactions when the MCR is formed via a six-membered ring transition state structure.[8−10] Apart from backbiting, intermolecular chain transfer to polymer (CTP) may also occur, contributing to the formation of high molecular weight polymer and gel fractions. CTP does not affect PLP measurements, which are carried out at low polymer concentration. Other hydrogen abstractions can occur during the side reaction between a growing polymer chain and a monomer, such as the so-called chain transfer to monomer (CTM).

Many studies established the high extent of CTP reactions in FRP of acrylates[11,12] whereas the presence of such reactions during FRP of BA has been recognized after spectrometric studies (^{13}C NMR) of its emulsion polymerization.[13,14] Furthermore, electron spin resonance (ESR) spectrometry studies have confirmed the existence of MCRs in acrylate polymerizations.[15−17] The established importance of intramolecular CTP in acrylate polymerization has triggered many experimental and computational investigations to study the associated kinetic parameters. Pre-exponential factors and

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activation energies have been reported for the polymerization of BA and are in good agreement despite the fact that they have been estimated using different approaches.[18−20] Although the measurement of transfer rate constants for such reactions is difficult experimentally, there exist data for the Arrhenius parameters associated with the CTM of butyl acrylate (BA) FRP in the literature.[21]

Recently, computational studies based on secondary reactions of alkyl acrylates have been published. In particular, CTM reactions have been studied using different computational methods[22] and the kinetics of the intramolecular interaction during FRP of BA[23] and of acrylate-based copolymers[24] have been estimated. To the best of our knowledge the only estimated values for the pre-exponential factor and activation energy of intermolecular CTP published in the literature are derived from mathematical models[25,26] and a study based on multidetector SEC measurements performed for BA in which the authors estimated the rate coefficient of intermolecular CTP for BA homopolymerization at 60 °C.[27]

All the above-mentioned reactions are hydrogen abstractions and are typical examples of reactions where quantum tunneling plays an important role. Quantum tunneling is the phenomenon in which a particle, or in this case a hydrogen atom, is able to tunnel through an energy barrier leading to higher rate coefficients. Quantum tunneling correction is relevant to the improvement of rate coefficient estimations for hydrogen abstraction reactions especially at typical temperature for FRP; thus the contribution of quantum tunneling must be accounted for. The addition of a proper coefficient that accounts for the quantum tunneling effect is of great importance because it may cause deviation of the kinetics of the reaction with respect to those predicted by the classical theory.[28]

In the present work a computational investigation of several hydrogen abstractions has been carried out. The aim was to provide an overview of the kinetics of bimolecular secondary reactions that involve hydrogen abstraction from a large number of chemical species present in a bulk free radical polymerization. The radical that was used for the study of the hydrogen abstraction reactions was a BA radical and its reactivity toward four different monomers (i.e., BA, BMA, VA, and ST) has been studied. In particular, BA has been used for the investigation of the hydrogen abstraction from the three different methylene and the methyl hydrogens from the butyl substituent group (reactions M in Figure 1). Butyl methacrylate (BMA), vinyl acetate (VA), and styrene (ST) have been used to study the abstractions of the methyl hydrogen next to the double bond (reaction B in Figure 1), the methyl hydrogen next to the carboxylic group (reaction V in Figure 1), and the three different methine hydrogens on the aromatic ring (reactions S in Figure 1), respectively.

The abstractions of methylene and methine hydrogen atoms from the vinyl group (reactions D in Figure 1) have been studied using both BA and VA monomers. For the study of hydrogen abstraction from a secondary and a tertiary carbon on the backbone chain (reactions P in Figure 2) the poly(butyl acrylate) (pBA), along with the copolymers poly(butyl acrylate-*co*-styrene) [p(BA-*co*-ST)] and poly(butyl acrylate-*co*-vinyl acetate) [p(BA-*co*-VA)] have been investigated. This study was aimed to enrich the existing results reported in the literature as well as to give an estimation of the kinetics for important side reactions that cannot be determined experimentally, taking into consideration the quantum tunneling effect. The knowledge of the kinetics of these reaction is of great importance because at high temperature they significantly affect the overall polymerization kinetics as well as the properties of the produced polymer.

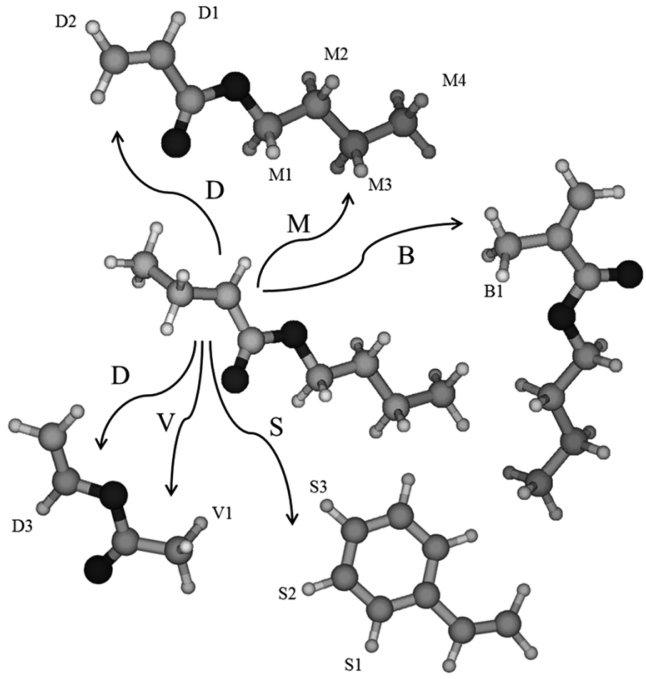

Figure 1. Studied hydrogen abstraction reactions from BA, VA, BMA, and ST monomers.

All kinetic coefficients are estimated according to the classical transition state theory using computational values obtained through density functional theory (DFT) methods with quantum tunneling factors estimated according to the Eckart model.

COMPUTATIONAL SECTION

Quantum mechanics (QM) approaches based on density functional theory have been used to investigate reactions that occur during FRP giving promising results.[29−32] There are few computational studies on intramolecular hydrogen abstraction in FRP of BA, ST, acrylonitrile, and vinyl chloride.[10,23,24,33−37] In the literature can be found a few studies underlining the importance of the quantum tunneling effect on hydrogen abstraction reactions in FRP,[33,34,36] whereas the relevance of this effect in this context has been investigated by Cuccato et al.[28]

In this study the exchange and correlation energies were calculated using a computational approach based on DFT. The Becke three-parameter Lee−Yang−Parr functional (B3LYP) has been used for the optimization of each reactant and product conformation whereas for the radicals the simulations were performed using a spin multiplicity of 2 and an unrestricted wave function (UB3LYP). Simulations were performed using the all electron 6-31 basis set with added polarization functions (6-31G(d,p)). There is a plenty of functional that may be used for the optimization of the geometries; however, the B3LYP method has been proved to provide excellent low-cost performance, as demonstrated in previous literature reports.[10,31,32,38−46] On the contrary, it is known that B3LYP is less accurate in predicting electronic energies compared to other hybrid density functionals,[47,48] and that was why a combined B3LYP/(6-31G(d,p))//MPWB1K/(6-31G(d,p))

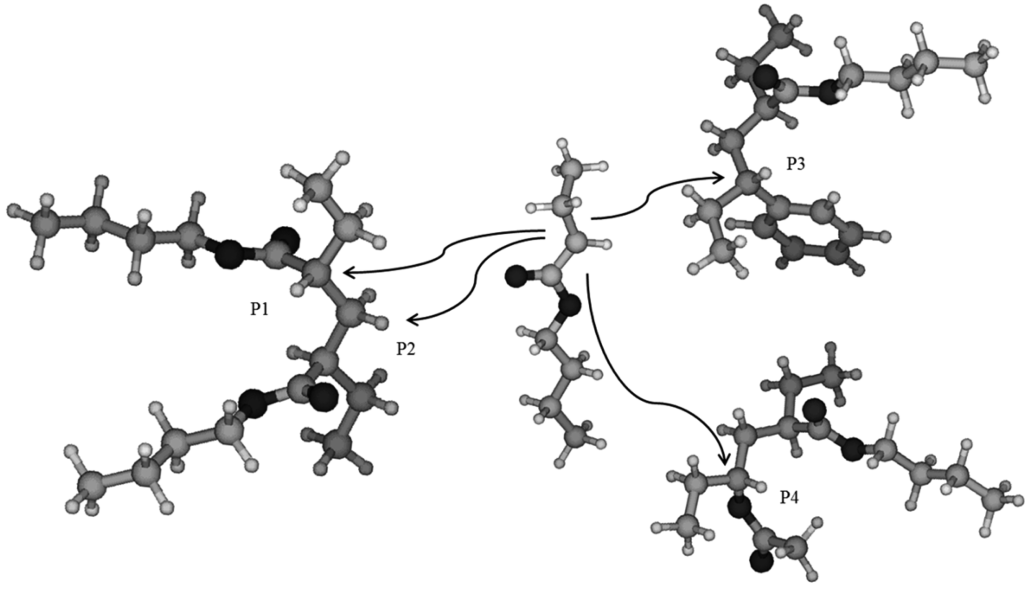

Figure 2. Studied hydrogen abstraction reactions from pBA, pBA-*co*-VA, and pBA-*co*-ST.

approach was used to estimate the kinetic constants. In particular, the geometries for each reactant, product and transition state that have been detected at the B3LYP level of theory were considered stable only after calculating the vibrational frequencies and force constants, as well as if no imaginary vibrational frequency was found. Transition state structures were located by adopting the synchronous transit-guided quasi Newton method and were characterized using a single imaginary vibrational frequency. After the geometric optimization the hybrid meta DFT method, MPWB1K was used to perform single point calculations to evaluate the electronic and zero-point energies.[49] The corresponding kinetic constants in both cases were determined using the classical transition state theory (TST) as follows:

$$k(T) = A \cdot e^{(-E_a/k_b T)} = \frac{k_b T}{h} \cdot \frac{Q^{\neq}}{Q^{R}} \cdot e^{(-E_a/k_b T)} \quad (1)$$

where k_b and h are the Boltzmann and Planck constants, respectively; in addition, T is the temperature, E_a is the activation energy of the process calculated from the difference between the electronic energy of the transition state and the energy of the reactants (including zero-point energy), and Q represents the product of the partition functions (q^{trans}, q^{vib}, q^{rot}, q^{el}) for the transition states ($\neq$) and reactants (R). In particular, q^{el} is the electronic partition function and q^{trans}, q^{vib}, and q^{rot} are the translational, vibrational, and rotational partition functions, respectively, calculated according to the following equations:

$$q^{trans} = \frac{(2\pi m k_b T)^{3/2}}{h^3} V \quad (2)$$

$$q^{vib} = \prod_{i=1}^{N_{vib}} \frac{1}{1 - \exp\left(-\frac{h\nu_i}{k_b T}\right)} \quad (3)$$

$$q^{rot} = \frac{8\pi^2 (2\pi k_b T)^{3/2} \sqrt{I_x I_y I_z}}{\sigma h^3} \quad (4)$$

where V is the volume, m is the particle mass, ν_i is the vibrational frequency, $I_x I_y I_z$ are the moments of inertia, and σ is the rotational symmetry number. The improvement of the estimated partition functions for the propagation reactions when the low vibrational frequencies are considered as internal rotations (hinder rotor approximation, HR) is well documented in the literature.[29,32,40,48] However, it has been shown that the provided improvement of the partition functions is less critical for hydrogen abstraction reactions at low temperatures. In particular, the use of the HR approximation provided estimation close to that obtained using the harmonic-oscillator (HO) approximation.[28] Because the studied reactions are hydrogen abstractions at low temperature the HO approximation has been applied.

The quantum tunneling effect can be introduced by multiplying the obtained kinetic coefficients for the bimolecular hydrogen abstraction by the quantum tunneling factor Q_{tun}, as shown in the eq 5. This factor is defined as the ratio between quantum and classical fluxes across the energy barrier and it can be calculated as in eq 6.

$$k(T)_{tun} = Q_{tun} k(T) \quad (5)$$

$$Q_{tun} = \frac{\int_0^{\infty} P(E) e^{(-E/k_b T)} \, dE}{\int_{E_1}^{\infty} e^{(-E/k_b T)} \, dE} \quad (6)$$

where $P(E)$ is the transmission probability. The analytical solution of the one-dimensional translational Schrödinger equation for the asymmetrical Eckart potential barrier has been used for the determination of the tunneling probability or transmission coefficient.[50] The Eckart model is less accurate than other more refined theories; however, it has been selected because it requires low computational effort. In particular, for the estimation of the quantum tunneling factors are required the activation energy and the imaginary frequency of the transition state. The difference for the predicted values by Eckart model and for those predicted using another more accurate method at the studied temperature is in the worst case a factor of 5.[28,51] The contribution of the imaginary frequency on quantum tunneling factor is of great importance, the bigger the absolute value of the imaginary frequency, the stronger the quantum tunneling effect. All of the quantum chemistry

Table 1. Estimated Values of the Activation Energy, Pre-exponential Factor, Quantum Tunneling Factor, Imaginary Frequency, and Rate Coefficient for the Bimolecular Hydrogen Abstractions[a]

	hydrogen abstraction reaction	E_A [kJ mol^{-1}]	$\log_{10}(A)$	Q_{tun}	frequency [cm^{-1}]	K [L mol^{-1} s^{-1}]
M1	from butyl group	57.4	5.240	26.69	1621.3i	4.03×10^{-4}
M2	from butyl group	60.1	5.487	15.16	1542.4i	1.40×10^{-4}
M3	from butyl group	62.1	6.062	19.48	1555.4i	3.00×10^{-4}
M4	from butyl group	75.8	6.631	15.21	1500.9i	3.36×10^{-6}
D1	from vinyl group	93.6	6.268	3.85	1249.4i	2.84×10^{-10}
D2	from vinyl group	98.6	5.890	2.97	1066.0i	1.20×10^{-11}
D3	from vinyl group	95.6	5.672	3.36	1174.4i	2.82×10^{-11}
P1	from tertiary carbon of the backbone	47.1	2.720	36.66	1667.3i	1.09×10^{-4}
P2	from secondary carbon of the backbone	67.1	3.474	35.93	1679.0i	1.88×10^{-7}
P3	from tertiary carbon of the backbone	61.3	3.599	68.86	1694.0i	4.89×10^{-6}
P4	from tertiary carbon of the backbone	69.8	3.683	37.94	*1682.5i*	1.08×10^{-7}
S1	from ortho position	95.5	5.391	3.78	1266.5i	1.74×10^{-11}
S2	from meta position	94.2	6.033	2.91	1110.0i	1.00×10^{-10}
S3	from para position	94.8	5.847	2.74	*1078.3i*	4.74×10^{-11}
B1	from methyl adjacent to vinyl group	59.7	5.739	49.70	*1650.4i*	9.39×10^{-4}
V1	from methyl adjacent to carboxylic group	67.1	5.960	19.15	*1524.0i*	3.10×10^{-5}

[a]Arrhenius parameters determined using the combined B3LYP/6-31G(d,p)//MPWB1K/6-31G(d,p) approach. Rate coefficients were calculated at 25 °C taking into consideration the quantum tunneling factor. (A) is reported as (L mol^{-1} s^{-1})

calculations were performed using the Gaussian 09 program suite and all pictures were drawn using Molden 4.2.[52,53]

RESULTS AND DISCUSSION

All the studied hydrogen abstraction reactions are divided into six groups, as shown in Figures 1 and 2. Specifically, group M refers to hydrogen abstraction reactions from the butyl substituent group of BA, group D includes the hydrogen abstractions from the vinyl groups of BA and VA, groups S, V, and B refer to hydrogen abstractions from ST, VA, and BMA monomers, respectively, and group P includes intermolecular secondary and tertiary hydrogen abstractions from pBA, p(BA-*co*-ST), and p(BA-*co*-VA) backbones.

Six CTM reactions have been studied for BA. In particular, the hydrogen abstractions from the methylene adjacent to the ester oxygen (M1), from the two internal methylene groups (M2, M3), and from the methyl group (M4) of the butyl substituent have been studied along with the abstractions from the methine (D1) and methylene (D2) hydrogens of the vinyl group. The mechanism of the ortho (S1), meta (S2), and para (S3) methine hydrogen abstractions has been studied using the ST monomer whereas the VA and the BMA monomers have been selected for the investigation of the hydrogen abstractions from the methyl group adjacent to the carboxylic (V1) and the vinyl group (B1), respectively. Additionally, the VA monomer has been selected to study the abstraction of the methine hydrogen adjacent to the oxygen (D3). Four CTP reactions have been investigated, namely, the hydrogen abstractions from the tertiary carbon (P1) and from the secondary carbon (P2) of the pBA backbone as well as the hydrogen abstraction from the tertiary carbon of the ST (P3) and VA (P4) units on the p(BA-*co*-ST) and p(BA-*co*-VA) backbones.

As can be seen in Figures 1 and 2, a methyl group has been added to the tail of the BA monomer radical to improve the chemical environment of the radical carbon such that the adjacent carbon is secondary like in a real propagating chain. Furthermore, to better mimic the polymer backbones shown in Figure 2, methyl and ethyl groups have been added at the ends of the dimer backbones to represent final molecules as dimers with a backbone composed of seven carbon atoms.

The determined activation energy values, pre-exponential factors, quantum tunneling factors, imaginary frequencies, and kinetic coefficients for the above-mentioned reactions are reported in the Table 1.

According to the computational results, the hydrogen abstraction from the methylene (M1) adjacent to an ester oxygen is the most favored reaction among the hydrogen abstractions from the butyl substituent group. This is in agreement with the theory because the presence of lone pair electrons on the oxygen atom is expected to increase the lability of the hydrogen atoms on the adjacent carbon atom. The predicted activation energies for the hydrogen abstraction reactions from the other methylene groups (M2 and M3) are slightly higher whereas the one for the hydrogen abstraction from the methyl group (M4) is almost 20 kJ/mol higher. There are almost no significant differences in the rate coefficients of the three methylene hydrogen abstractions, whereas the rate constants for the methyl hydrogen abstraction is 2 orders of magnitude lower. The results for the methylene abstractions contradict a previous study in which the authors claim that the products of hydrogen abstraction reactions from the two middle methylene group (M2, M3) of the butyl pendant are thermodynamically favored.[54] Furthermore, the computational results of this work are in agreement with a recently published study that claims there is no significant difference in activation energies or in kinetic coefficients for all the methylene hydrogen abstractions.[22]

Experimental values of activation energies for similar hydrogen abstractions are reported in literature and they are in agreement with the computational values for abstraction of methylene and methyl hydrogen reported in this work. In particular, Mintz et al. report that the hydrogen abstraction from the methylene group of propane by a methyl radical is characterized by an activation energy of 55.5 kJ/mol, which is lower than the 62.4 kJ/mol for the abstraction from the methyl group,[55] whereas in another study the latter abstraction is reported as 73.3 kJ/mol.[56] The hydrogen abstraction from a carbon adjacent to an oxygen has been studied for methanol[57] and ethanol[58] and in both cases the values confirm that the presence of the lone pairs on the adjacent oxygen leads to lower

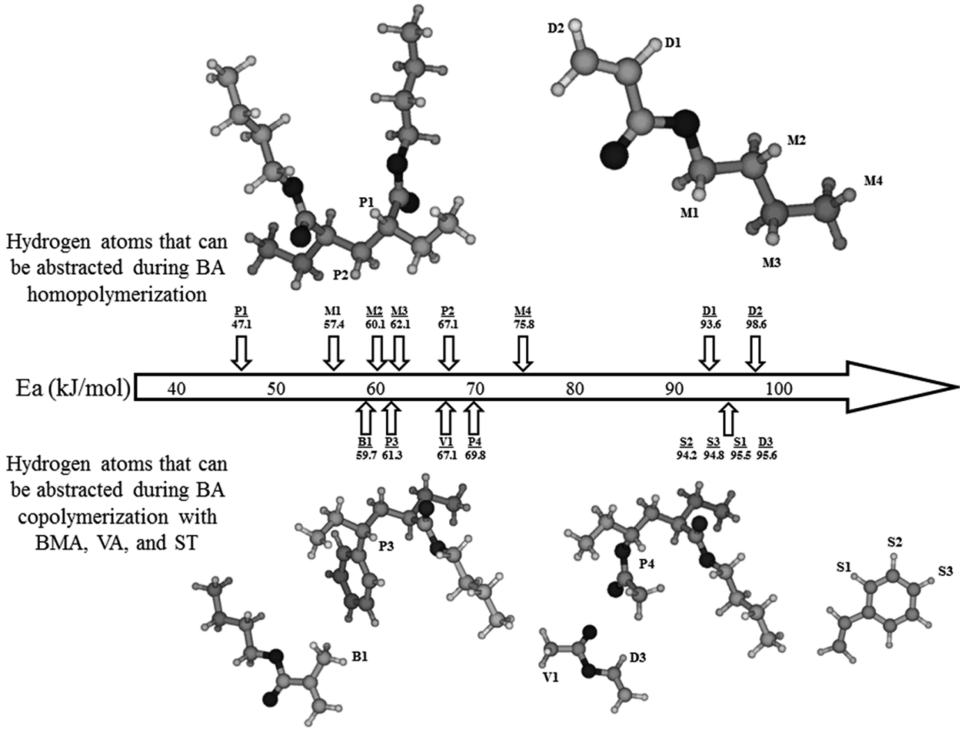

Figure 3. Comparison of required activation energy values for hydrogen abstraction reactions during the homopolymerization as well as the copolymerization of BA with BMA, VA, and ST.

activation energies for the methylene hydrogen abstractions (40−44 kJ/mol). On the other hand, the differences between the experimental data and the computationally estimated kinetic parameters are rather large. This evidence holds even for the determination of backbiting rate coefficients. In our recent work,[23] the computed activation energy for the backbiting 1:5 reaction is larger than the experimental one. Interestingly, the experimentally estimated values of activation energies of backbiting and CTM events are close to each other (i.e., 32−35 kJ/mol[5,18] vs 33 kJ/mol[21]) as it happens for computations (i.e., 55 kJ/mol[23] vs 57 kJ/mol, this work). These evidences clearly prove the presence of a systematic error in the computation of an absolute kinetic constant value leading to the already reported conclusion that the use of QM is more reliable when kinetic constants ratio is provided.

As expected, all the hydrogen abstractions of methine (D1) and methylene (D2) hydrogens on the vinyl group of BA monomer and of methine hydrogen (D3) on the vinyl group of VA monomer were found to be less favored. These reactions that involve a hydrogen abstraction from an sp^2 carbon exhibit high activation energies, about 95 kJ/mol, and kinetic rate constants at least 4 orders of magnitude lower compared to the abstractions from the butyl substituent group. The kinetic values reported in Table 1 for the hydrogen abstraction of ortho, meta, and para aromatic hydrogens from the ST monomer (S1, S2, and S3) are of the same order of magnitude as those of group D reactions, confirming once again that there is a high energy barrier associated with the abstraction of a hydrogen atom from an sp^2 carbon; accordingly, the activation energy values range from 62 to 73 kJ/mol for hydrogen abstraction from ethylene, as reported in the literature.[59−61] A comparison between the activation energies and the kinetic coefficients for the abstraction of the methyl hydrogen for the reactions B1 and V1 as well as those estimated for the reaction M4 once again confirmed the importance of the chemical environment in the abstraction kinetics. Both of the above-mentioned abstractions were expected to have lower activation energies than the M4 abstraction because they possess a weaker electron donor group (B1) or an electron withdrawing group (V1) close to the abstracted hydrogen atom. Indeed, the calculated activation energies were lower. However, an interesting observation is made when the activation energies of the V1 and B1 abstractions are compared to each other. In particular, the presence of the electron donor group seems to lead to a lower activation energy than the presence of the electron withdrawing group, which is in contrast to the expectations according to theory. Nonetheless, this may be explained by the mesomeric effect as there are two resonance structures for the radical generated after the B1 abstraction that stabilize the produced radical, leading to a lower activation energy for the abstraction.

The results for the CTP reactions (group P) reported in Table 1 show that the hydrogen abstraction from a tertiary carbon on pBA backbone (P1) is characterized by an activation energy 20 kJ/mol lower than that from a secondary carbon on the same backbone (P2). The estimated value for the activation energy of reaction P1 is the lowest among all the investigated reactions. This evidence can be explained because the radical on the tertiary carbon produced after the hydrogen abstraction is the most stable radical among those studied. The difference in estimated pre-exponential factors for the CTP (group P) and CTM (group M) reactions in Table 1 is more than 2 orders of magnitude and it is in agreement with previously reported data.[21,25] The chemical environment close to the tertiary carbon plays a relevant role in the hydrogen abstraction reactions. In particular, the abstraction activation energy increases from an electron withdrawing (P1) to a weak (P3) and strong (P4) electron donor moiety. A schematic of the

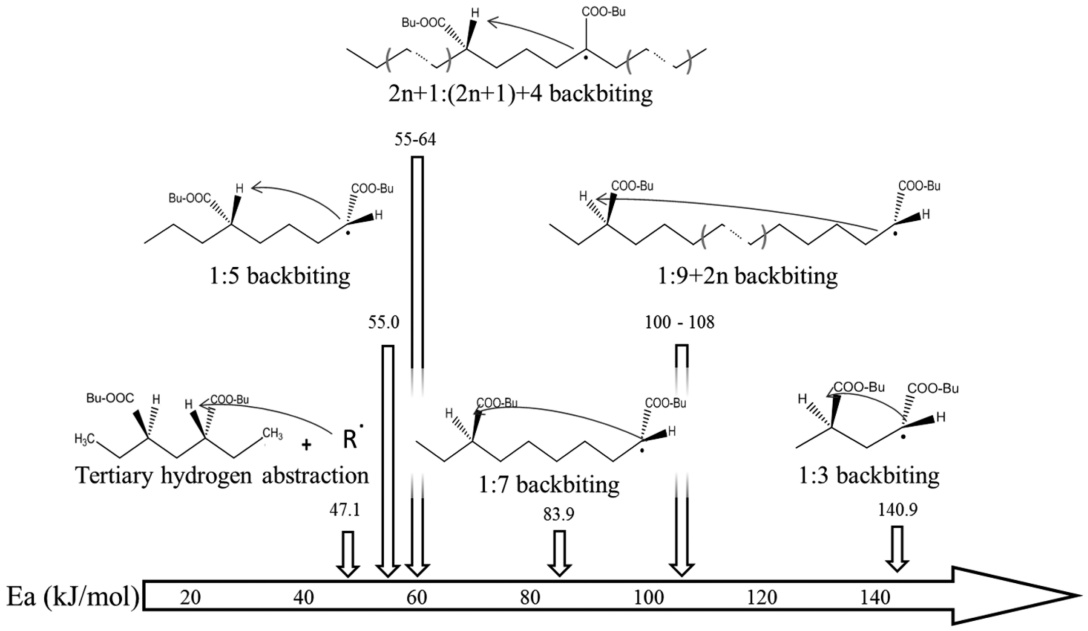

Figure 4. Comparison of required activation energy values for inter- and intramolecular[23] hydrogen abstraction from tertiary carbon.

increasing activation energies for the studied CTM and CTP reactions are illustrated in Figure 3.

Furthermore, it is interesting to compare the activation energies for CTP reactions estimated in this work to recent published values for the activation energies of backbiting reaction estimated at the same level of theory and temperature for the same polymer system[23] (Figure 4). The estimated activation energy for the intermolecular hydrogen abstraction from the tertiary carbon (P1) on the polymer backbone is lower than those reported for the 1:j (with j = 3, 5, 7, 9, 11, and 13) as well as for the internal backbiting reactions. This result was expected because the intermolecular hydrogen abstraction does not require the formation of a ring configuration, whereas for intramolecular reactions ring is necessary and accordingly the required activation energies increase (ring strain).

The activation energy for the intermolecular hydrogen abstraction from a secondary carbon (P2) is higher than the ones of the above-mentioned 1:5 and $2n$ + 1:($2n$ + 1) + 4 backbating events, which require the formation of a six-membered ring transition state. On the contrary, when the six ring transition state is not present (1:3, 1:7, 1:9, etc.) the activation energy for the backbiting reaction is higher.

A last comment should be made regarding the effect of the imaginary frequency values on the tunneling factors. As mentioned in the Introduction, the contribution of the imaginary frequency to the tunneling factor is of great importance, and the values in Table 1 confirmed it. The reactions D1, D2, D3, S1, S2, and S3 have low imaginary frequency values with consequent low quantum tunneling factors. For these reactions the tunneling effect can be considered negligible. On the contrary, the quantum tunneling factors give an important contribution for the hydrogen abstraction reactions from an sp^3 carbon at mild temperature. That contribution for specific reactions (i.e., reactions P1, P2, P3, P4, and B1) can be a factor of 30 or greater.

CONCLUSION

A quantum chemical investigation of bimolecular hydrogen abstractions in free radical polymerization on butyl acrylate-based systems has been conducted. The study was focused on the specification of the contribution of the chemical environment and the tunneling effect on the determination of the reaction kinetics. Various bimolecular reactions were investigated at the B3LYP/6-31G(d,p)//MPWB1K/6-31G(d,p) level of theory with the tunneling correction calculated adopting Eckart model and the kinetic coefficients were evaluated at 25 °C. It was found that the chemical environment can both promote and prevent the adjacent hydrogen abstraction. The quantum tunneling effect has been proven to be of great importance because it can enhance the hydrogen abstraction. For some of the studied reactions the quantum tunneling factor was greater than 20 at mild polymerization temperature. The estimated activation energy for the intermolecular abstraction of a hydrogen atom from a tertiary carbon on the polymer backbone was lower than that for the intramolecular abstraction of the same hydrogen as it was expected. The computational approach can lead to detailed estimations for the kinetics of reactions, which are hard to study experimentally and may help for the better understanding of the overall kinetic scheme of FRP. In the present study it was found that the most favorable hydrogen abstraction reaction is the CTP where a tertiary hydrogen is abstracted by a BA unit on the backbone. CTM reactions promoted by electron donors (M1) or by mesomeric effect (B1) follow, whereas the less favorable chain transfer reactions are associated with abstraction from an sp^2 carbon.

ASSOCIATED CONTENT

Supporting Information

Detail of the atom coordinates of the optimized transition state structures corresponding to the investigated reactions reported in Table 1. This material is available free of charge via Internet.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PLP, pulsed laser polymerization; SEC, size exclusion chromatography; CER, chain-end radicals; MCR, midchain radicals; CTM, chain transfer to monomer; CTP, chain transfer to polymer; FRP, free radical polymerization; BA, butyl acrylate; NMR, nuclear magnetic resonance; ESR, electron spin resonance; BMA, butyl methacrylate; VA, vinyl acetate; ST, styrene; DFT, density functional theory; QM, quantum mechanics; TST, transition state theory

■ REFERENCES

(1) Buback, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F. D.; Manders, B. G.; Odriscoll, K. F.; Russell, G. T.; Schweer, J. Critically Evaluated Rate Coefficients for Free-Radical Polymerization. 1. Propagation Rate Coefficient for Styrene. *Macromol. Chem. Phys.* **1995**, *196*, 3267.

(2) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; Odriscoll, K. F.; Shen, J.; Winnik, M. A. Consistent Values of Rate Parameters in Free Radical Polymerization Systems. 2 Outstanding Dilemmas and Recommendations. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 851.

(3) Beuermann, S.; Paquet, D. A.; McMinn, J. H.; Hutchinson, R. A. Determination of free-radical propagation rate coefficients of butyl, 2-ethylhexyl, and dodecyl acrylates by pulsed-laser polymerization. *Macromolecules* **1996**, *29*, 4206.

(4) Lyons, R. A.; Hutovic, J.; Piton, M. C.; Christie, D. I.; Clay, P. A.; Manders, B. G.; Kable, S. H.; Gilbert, R. G. Pulsed-laser polymerization measurements of the propagation rate coefficient for butyl acrylate. *Macromolecules* **1996**, *29*, 1918.

(5) Nikitin, A. N.; Hutchinson, R. A.; Buback, M.; Hesse, P. Determination of intramolecular chain transfer and midchain radical propagation rate coefficients for butyl acrylate by pulsed laser polymerization. *Macromolecules* **2007**, *40*, 8631.

(6) Barth, J.; Buback, M.; Hesse, P.; Sergeeva, T. EPR Analysis of n-Butyl Acrylate Radical Polymerization. *Macromol. Rapid Commun.* **2009**, *30*, 1969.

(7) Junkers, T.; Barner-Kowollik, C. The Role of Mid-Chain Radicals in Acrylate Free Radical Polymerization: Branching and Scission. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7585.

(8) Roedel, M. J. The Molecular Structure of Polyethylene. I. Chain Branching in Polyethylene during Polymerization1. *J. Am. Chem. Soc.* **1953**, *75*, 6110.

(9) Toh, J. S. S.; Huang, D. M.; Lovell, P. A.; Gilbert, R. G. Ab initio calculation of the rate coefficient for short-chain branching in free-radical polymerizations. *Polymer* **2001**, *42*, 1915.

(10) Moscatelli, D.; Cavallotti, C.; Morbidelli, M. Prediction of molecular weight distributions based on ab initio calculations: Application to the high temperature styrene polymerization. *Macromolecules* **2006**, *39*, 9641.

(11) Ahmad, N. M.; Britton, D.; Heatley, F.; Lovell, P. A. Chain transfer to polymer in emulsion polymerization. *Macromol. Symp.* **1999**, *143*, 231.

(12) Heatley, F.; Lovell, P. A.; Yamashita, T. Chain transfer to polymer in free-radical solution polymerization of 2-ethylhexyl acrylate studied by NMR spectroscopy. *Macromolecules* **2001**, *34*, 7636.

(13) Lovell, P. A.; Shah, T. H.; Heatley, F. Chain Transfer to Polymer in Emulsion Polymerization of Normal-Butyl Acrylate Studied by C-13 NMR Spectroscopy and GPC. *Polym. Commun.* **1991**, *32*, 98.

(14) Ahmad, N. M.; Charleux, B.; Farcet, C.; Ferguson, C. J.; Gaynor, S. G.; Hawkett, B. S.; Heatley, F.; Klumperman, B.; Konkolewicz, D.; Lovell, P. A.; Matyjaszewski, K.; Venkatesh, R. Chain Transfer to Polymer and Branching in Controlled Radical Polymerizations of n-Butyl Acrylate. *Macromol. Rapid Commun.* **2009**, *30*, 2002.

(15) Yamada, B.; Azukizawa, M.; Yamazoe, H.; Hill, D. J. T.; Pomery, P. J. Free radical polymerization of cyclohexyl acrylate involving interconversion between propagating and mid-chain radicals. *Polymer* **2000**, *41*, 5611.

(16) Gilbert, B. C.; Smith, J. R. L.; Milne, E. C.; Whitwood, A. C.; Taylor, P. Kinetic and Structural EPR Studies of Radical Polymerization - Monomer, Dimer, Trimer and Midchain Radicals Formed via the Initiation of Polymerization of Acrylic-Acid and Related-Compounds With Electrophilic Radicals. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1759.

(17) Azukizawa, M.; Yamada, B.; Hill, D. J. T.; Pomery, P. J. Radical polymerization of phenyl acrylate as studied by ESR spectroscopy: concurrence of propagating and mid-chain radicals. *Macromol. Chem. Phys.* **2000**, *201*, 774.

(18) Barth, J.; Buback, M.; Hesse, P.; Sergeeva, T. Termination and Transfer Kinetics of Butyl Acrylate Radical Polymerization Studied via SP-PLP-EPR. *Macromolecules* **2010**, *43*, 4023.

(19) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; van Herk, A. M.; Leiza, J. R.; Asua, J. M. Evidence of branching in poly(butyl acrylate) produced in pulsed-laser polymerization experiments. *Macromol. Rapid Commun.* **2003**, *24*, 173.

(20) Nikitin, A. N.; Hutchinson, R. A.; Wang, W.; Kalfas, G. A.; Richards, J. R.; Bruni, C. Effect of Intramolecular Transfer to Polymer on Stationary Free-Radical Polymerization of Alkyl Acrylates, 5-Consideration of Solution Polymerization up to High Temperatures. *Macromol. React. Eng.* **2010**, *4*, 691.

(21) Maeder, S.; Gilbert, R. G. Measurement of transfer constant for butyl acrylate free-radical polymerization. *Macromolecules* **1998**, *31*, 4410.

(22) Moghadam, N.; Liu, S.; Srinivasan, S.; Grady, M. C.; Soroush, M.; Rappe, A. M. Computational Study of Chain Transfer to Monomer Reactions in High-Temperature Polymerization of Alkyl Acrylates. *J. Phys. Chem. A* **2013**, *117*, 2605.

(23) Cuccato, D.; Mavroudakis, E.; Dossi, M.; Moscatelli, D. A Density Functional Theory Study of Secondary Reactions in n-Butyl Acrylate Free Radical Polymerization. *Macromol. Theory Simul.* **2013**, *22*, 127.

(24) Cuccato, D.; Mavroudakis, E.; Moscatelli, D. Quantum Chemistry Investigation of Secondary Reaction Kinetics in Acrylate-Based Copolymers. *J. Phys. Chem. A* **2013**, *117*, 4358.

(25) Plessis, C.; Arzamendi, G.; Leiza, J. R.; Schoonbrood, H. A. S.; Charmot, D.; Asua, J. M. Modeling of seeded semibatch emulsion polymerization of n-BA. *Ind. Eng. Chem. Res.* **2001**, *40*, 3883.

(26) Arzamendi, G.; Plessis, C.; Leiza, J. R.; Asua, J. M. Effect of the intramolecular chain transfer to polymer on PLP/SEC experiments of alkyl acrylates. *Macromol. Theory Simul.* **2003**, *12*, 315.

(27) Boschmann, D.; Vana, P. Z-RAFT star polymerizations of acrylates: Star coupling via intermolecular chain transfer to polymer. *Macromolecules* **2007**, *40*, 2683.

(28) Cuccato, D.; Dossi, M.; Polino, D.; Cavallotti, C.; Moscatelli, D. Is Quantum Tunneling Relevant in Free-Radical Polymerization? *Macromol. React. Eng.* **2012**, *6*, 496.

(29) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. A priori prediction of propagation rate coefficients in free-radical polymerizations: Propagation of ethylene. *Macromolecules* **1995**, *28*, 8771.

(30) Fischer, H.; Radom, L. Factors controlling the addition of carbon-centered radicals to alkenes-an experimental and theoretical perspective. *Angew. Chem., Int. Ed.* **2001**, *40*, 1340.

(31) Van Speybroeck, V.; Van Cauter, K.; Coussens, B.; Waroquier, M. Ab initio study of free-radical polymerizations: Cost-effective methods to determine the reaction rates. *Chemphyschem* **2005**, *6*, 180.

(32) Izgorodina, E. I.; Coote, M. L. Accurate ab initio prediction of propagation rate coefficients in free-radical polymerization: Acrylonitrile and vinyl chloride. *Chem. Phys.* **2006**, *324*, 96.

(33) Pfaendtner, J.; Yu, X. R.; Broadbelt, L. J. Quantum chemical investigation of low-temperature intramolecular hydrogen transfer reactions of hydrocarbons. *J. Phys. Chem. A* **2006**, *110*, 10863.
(34) Purmova, J.; Pauwels, K. F. D.; Agostini, M.; Bruinsma, M.; Vorenkamp, E. J.; Schouten, A. J.; Coote, M. L. Experimental and theoretical evaluation of the reactions leading to formation of internal double bonds in suspension PVC. *Macromolecules* **2008**, *41*, 5527.
(35) Van Cauter, K.; Van den Bossche, B. J.; Van Speybroeck, V.; Waroquier, M. Ab initio study of free-radical polymerization: Defect structures in poly(vinyl chloride). *Macromolecules* **2007**, *40*, 1321.
(36) Cuccato, D.; Dossi, M.; Moscatelli, D.; Storti, G. Quantum Chemical Investigation of Secondary Reactions in Poly(vinyl chloride) Free-Radical Polymerization. *Macromol. React. Eng.* **2012**, *6*, 330.
(37) Cuccato, D.; Dossi, M.; Moscatelli, D.; Storti, G. A Density Functional Theory Study of Poly (vinyl chloride) (PVC) Free Radical Polymerization. *Polym. React. Eng. - 10th Int. Workshop* **2011**, 100.
(38) Dossi, M.; Liang, K.; Hutchinson, R. A.; Moscatelli, D. Investigation of Free-Radical Copolymerization Propagation Kinetics of Vinyl Acetate and Methyl Methacrylate. *J. Phys. Chem. B* **2010**, *114*, 4213.
(39) Dossi, M.; Storti, G.; Moscatelli, D. Initiation Kinetics in Free-Radical Polymerization: Prediction of Thermodynamic and Kinetic Parameters Based on ab initio Calculations. *Macromol. Theory Simul.* **2010**, *19*, 170.
(40) Van Speybroeck, V.; Van Neck, D.; Waroquier, M.; Wauters, S.; Saeys, M.; Marin, G. B. Ab initio study of radical addition reactions: Addition of a primary ethylbenzene radical to ethene (I). *J. Phys. Chem. A* **2000**, *104*, 10939.
(41) Wong, M. W.; Radom, L. Radical addition to alkenes: Further assessment of theoretical procedures. *J. Phys. Chem. A* **1998**, *102*, 2237.
(42) Gomez-Balderas, R.; Coote, M. L.; Henry, D. J.; Radom, L. Reliable theoretical procedures for calculating the rate of methyl radical addition to carbon-carbon double and triple bonds. *J. Phys. Chem. A* **2004**, *108*, 2874.
(43) Peng, C. Y.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. Using redundant internal coordinates to optimize equilibrium geometries and transition states. *J. Comput. Chem.* **1996**, *17*, 49.
(44) Moscatelli, D.; Dossi, M.; Cavallotti, C.; Storti, G. Density Functional Theory Study of Addition Reactions of Carbon-Centered Radicals to Alkenes. *J. Phys. Chem. A* **2011**, *115*, 52.
(45) Mavroudakis, E.; Liang, K.; Moscatelli, D.; Hutchinson, R. A. A Combined Computational and Experimental Study on the Free-Radical Copolymerization of Styrene and Hydroxyethyl Acrylate. *Macromol. Chem. Phys.* **2012**, *213*, 1706.
(46) Dossi, M.; Storti, G.; Moscatelli, D. Relevance of Backbiting and Beta-Scission Reactions in the Free Radical Polymerization of Acrylonitrile. *Macromol. Symp.* **2010**, *289*, 119.
(47) Hemelsoet, K.; Moran, D.; Van Speybroeck, V.; Waroquier, M.; Radom, L. An assessment of theoretical procedures for predicting the thermochemistry and kinetics of hydrogen abstraction by methyl radical from benzene. *J. Phys. Chem. A* **2006**, *110*, 8942.
(48) Yu, X. R.; Pfaendtner, J.; Broadbelt, L. J. Ab initio study of acrylate polymerization reactions: Methyl methacrylate and methyl acrylate propagation. *J. Phys. Chem. A* **2008**, *112*, 6772.
(49) Zhao, Y.; Truhlar, D. G. Hybrid meta density functional theory methods for thermochemistry, thermochemical kinetics, and non-covalent interactions: The MPW1B95 and MPWB1K models and comparative assessments for hydrogen bonding and van der Waals interactions. *J. Phys. Chem. A* **2004**, *108*, 6908.
(50) Eckart, C. The Penetration of a Potential Barrier by Electrons. *Phys. Rev.* **1930**, *35*, 1303.
(51) Sirjean, B.; Dames, E.; Wang, H.; Tsang, W. Tunneling in Hydrogen-Transfer Isomerization of n-Alkyl Radicals. *J. Phys. Chem. A* **2011**, *116*, 319.
(52) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision B.01; Gaussian, Inc.: Wallingford, CT, 2009.
(53) Schaftenaar, G.; Noordik, J. H. Molden: a pre- and post-processing program for molecular and electronic structures. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123.
(54) Sangster, D. F.; Feldthusen, J.; Strauch, J.; Fellows, C. M. Measurement of transfer coefficients to monomer for n-butyl methacrylate by molecular weight distributions from emulsion polymerization. *Macromol. Chem. Phys.* **2008**, *209*, 1612.
(55) Mintz, K. J.; Le Roy, D. J. Kinetics of radical reactions in sodium diffusion flames. *Can. J. Chem.* **1978**, *56*, 941.
(56) Leathard, D. A.; Purnell, J. H. Propyl Radical Isomerization and Heterogeneous Effects in the Pyrolysis of Propane Below 500 °C. *Proc. R. Soc. London, Ser. A: Math. Phys. Sci.* **1968**, *306*, 553.
(57) Shannon, T. W.; Harrison, A. G. The reaction of methyl radicals with methy alcohol. *Can. J. Chem.* **1963**, *41*, 2455.
(58) Gray, P.; Herod, A. A. Methyl radical reactions with ethanol and deuterated ethanols. *Trans. Faraday Soc.* **1968**, *64*, 1568.
(59) Zhang, H. X.; Back, M. H. Rate constants for abstraction of hydrogen from ethylene by methyland ethyl radicals over the temperature-range 650−770K. *Int. J. Chem. Kinet.* **1990**, *22*, 21.
(60) Ahonkhai, S. I.; Lin, X. H.; Back, M. H. Rate constants for abstraction of hydrogen from ethylene by methyl and ethyl radicals relative to abstraction from propane and isobutane. *Int. J. Chem. Kinet.* **1989**, *21*, 1.
(61) Ahonkhai, S. I.; Back, M. H. Relative rate constants for abstraction of hydrogen by methyl radicals from ethane and from ethylene. *Can. J. Chem.* **1988**, *66*, 578.