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Quantum Chemical Investigation of the Mechanism of Direct Initiation of Isobutylene Polymerization by Boron Trichloride[†]

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ABSTRACT: Quantum chemical calculations by the MNDO and PM-3 methods, taking into account nonspecific solvation effects, were carried out in order to elucidate the mechanism of direct initiation of living carbocationic polymerization of isobutylene (IB) by BCl_3. Enthalpies and activation energies obtained by these investigations are consistent with direct addition of BCl_3 to IB (chloroboration) in polar solvents like CH_3Cl and CH_2Cl_2. These calculations also suggest that the ion generation reaction proceeds between excess of BCl_3 and the product of the chloroboration reaction ($Cl_2BCH_2C(CH_3)_2Cl$, **III**), leading to an ion pair, $Cl_2BCH_2C(CH_3)_2{}^+BCl_4{}^-$ (**IV**). Addition of IB (initiation) to such an ion pair was shown to be more probable than that to a zwitterionic intermediate ($Cl_3B^-CH_2C(CH_3)_2{}^+$, **I**), which may be formed in the first stage of the chloroboration reaction. It was found that the MNDO method gives three local minima of **IV** having different orientations of the $BCl_4{}^-$ counterion in polar solvent and interionic distances (R) in the range of 4.6−6.1 Å. This indicates that a real value for R can be found in this range. The propagation enthalpy values (ΔH_p) of IB polymerization obtained by the MNDO calculations are higher by 20−22 kcal/mol than the experimental value of $\Delta H_p = -17.2$ kcal/mol. This difference is attributed to the tendency of overestimating the repulsion between nonbonded atoms by the MNDO method. PM-3 calculations, free from this problem, gave ΔH_p in good agreement with the experimental data.

Introduction

The rapid advances in the field of living carbocationic polymerization (LCCP) of vinyl monomers have attracted worldwide interest in recent years. LCCP provides a wide variety of new polymeric materials, such as macromonomers, exact telechelics, polymers with pendant functional groups (liquid crystalline homo- and copolymers, nonlinear optical materials etc.), star-shaped macromolecules, block and graft copolymers, cyclic macromolecules, and several specialty networks (for recent reviews, see refs 1−5). Telechelic polymers, i.e., polymer chains with reactive termini, are of special importance as building blocks of macromolecular systems in many fundamental investigations and industrial applications. It has been recently found that BCl_3 induces LCCP of isobutylene (IB) in polar solvents such as CH_3Cl and CH_2Cl_2, and it leads to asymmetric telechelic poly(isobutylene) (PIB) with $Cl_2BCH_2C(CH_3)_2-$ headgroup and a tertiary chlorine ($-CH_2C(CH_3)_2Cl$) endgroup.[6] Analysis of the kinetics of IB consumption[7] indicated that initiation of IB polymerization can be assumed to occur by a two-step process: (1) direct addition of BCl_3 to IB, forming $Cl_2BCH_2C(CH_3)_2Cl$, and (2) reaction of this product with another BCl_3 molecule, resulting in a carbocationic species able to initiate LCCP of IB:

$$BCl_3 + CH_2{=}C(CH_3)_2 \rightarrow Cl_2BCH_2C(CH_3)_2Cl \quad (1)$$

$$Cl_2BCH_2C(CH_3)_2Cl + BCl_3 \rightleftarrows Cl_2BCH_2C^+(CH_3)_2BCl_4{}^- \quad (2)$$

Recently, semiempirical quantum chemical investigations[8] have revealed the possibility of formation of a zwitterionic structure between BCl_3 and propylene, which can be viewed as a simplified model of olefins in carbocationic polymerization. It has been found that the zwitterionic complex between BCl_3 and propylene is able to participate in the propagation step, but it can also be an intermediate in the haloboration reaction.[8] In this work, a more detailed quantum chemical study is carried out to consider the possible interactions between BCl_3 and IB in relation to the proposed initiation and polymerization mechanism[6] in this system.

Methods

All calculations have been carried out using the semiempirical MNDO[9] and PM-3 methods[10] implemented in the MOPAC 6.0 program. The geometries of all studied compounds have been completely optimized using the eigenvector following (EF) procedure. Calculations of the energy of nonspecific solvation by the solvent as a dielectric continuum were carried out with a specially designed version of the MOPAC 6.0 program.[11] According to this approach used for the nonspecific solvation energy calculations, a solute molecule is placed into a cavity within the dielectric continuum, this cavity being formed by intersecting van der Waals spheres of the atoms of the solute molecule. The reaction field of the dielectric continuum induced by the solute charge distribution is determined self-consistently, i.e., the polarization of the medium by the solute charge distribution and the reverse polarization of the solute by the polarized medium are taken into account.[11] The dielectric constant of the solvent was taken as $\epsilon = 12.0$, similar to those of CH_3Cl and CH_2Cl_2 at usual polymerization temperatures (−70 to −80 °C).[12] The calculations for the nonspecific solvation energy were carried out at the geometries of the compounds optimized in vacuum. Since the interionic distance in ion pairs may be considerably longer in polar solvents compared to that in vacuum, the influence

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[†] This study is dedicated to the memory of Dr. G. E. Chudinov, deceased suddenly in 1994.

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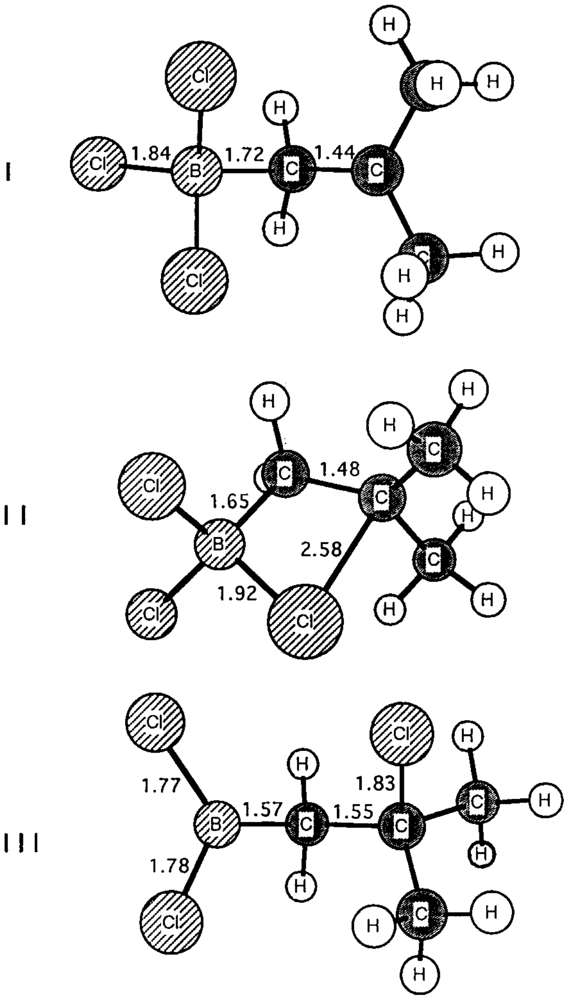


Figure 1. Completely optimized vacuum geometry of zwitterionic intermediate **I**, transition state **II**, and product **III** of chloroboration of isobutylene. Interatomic distances are presented in angstroms.

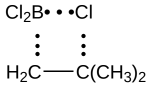
of polar solvent on the interionic distances and energies for ion pairs was also estimated.

Results and Discussion

Chloroboration of Isobutylene. MNDO calculations indicate that, as in the case of the addition of BCl_3 to propylene,[8] a zwitterionic covalently bound complex (**I**) formed between BCl_3 and IB is stable, i.e., it corresponds to a local minimum of the potential energy surface:

$$CH_2{=}C(CH_3)_2 + BCl_3 \rightarrow \underset{\textbf{(I)}}{Cl_3B^-CH_2C^+(CH_3)_2}$$

The completely optimized geometries of the transition state **II** of the chloroboration reaction (eq 1) and the product **III** of this reaction were also determined. The



$$\begin{array}{ccc} Cl_2B & \cdots & Cl \\ \vdots & & \vdots \\ H_2C & \text{—} & C(CH_3)_2 \end{array}$$

(II)

$Cl_2BCH_2C(CH_3)_2Cl$

(III)

geometries for structures **I**–**III** are shown in Figure 1.

The minimized heats of formation (ΔH_f) for structures **I**–**III** are presented in Table 1 for two values of dielectric constants (ϵ) of the medium (1 for vacuum and 12 for polar solvent, such as CH_3Cl and CH_2Cl_2). Table 1 also shows the ΔH_f values for BCl_3 and IB used for obtaining the activation energy ($\Delta E^{\ddagger}$) of the chloroboration reaction and the enthalpies (ΔH) of the zwitterionic intermediate **I** and the chloroboration product **III** with respect to the isolated BCl_3 and IB molecules. As the data indicate in this table, nonspecific solvation gives rise to a considerable stabilization of the zwitterionic intermediate **I** and transition state **II** of the chloroboration reaction. As a result, the ΔH and $\Delta E^{\ddagger}$ values calculated for $\epsilon = 12$ are as low as 8.0 and 10.1 kcal/mol, respectively. The ΔH values for the formation of **III** from IB and BCl_3 change from 2.5 to 0.6 kcal/mol upon the transition from vacuum to polar medium, i.e., the chloroboration reaction becomes nearly thermoneutral in the polar solvent according to the MNDO calculations. These quantum chemical data indicate that the direct chloroboration reaction leading to **III** may quite easily proceed in polar solvents, which is in agreement with experimental findings.[6]

Table 1. MNDO-Calculated Values of ΔH_f for Structures I–VI and Enthalpies of Reactions of Their Formation (ΔH for the Local Minima Structures I, III–VI, and $\Delta E^{\ddagger}$ for the Transition State II)

compound	ϵ	ΔH_f (kcal/mol)	ΔH (kcal/mol)	$\Delta E^{\ddagger}$ (kcal/mol)	reactions
I	1	−67.0	22.2		IB + BCl_3
	12	−81.6	8.0		
II	1	−62.9		26.3	IB + BCl_3
	12	−79.5		10.1	
III	1	−86.7	2.5		IB + BCl_3
	12	−89.0	0.6		
IV	1	−139.1	35.0		**III** + BCl_3
	12	−165.9	10.7		
V	1	−31.3	37.5		**I** + IB
	12	−70.5	13.1		
VI	1	−139.6	1.3		**IV** + IB
	12	−167.9	0.0		
BCl_3	1	−87.4			
	12	−87.6			
BCl_4^-	1	−199.5			
	12	−246.4			
IB	1	−1.8			
	12	−2.0			

Ion Generation. An initiator of the subsequent IB polymerization can be either an ion pair (**IV**) formed from **III** and excess BCl_3 (eq 3) or the zwitterionic intermediate **I**. Elimination in the presence of BCl_3 was

$$\textbf{III} + BCl_3 \rightarrow \underset{\textbf{(IV)}}{Cl_2BCH_2C^+(CH_3)_2/BCl_4^-} \qquad (3)$$

not taken into account due to the fact that BCl_3-coinitiated polymerization of IB is free from chain transfer under conditions usually used in practice, i.e., elimination is absent. The ΔH_f values and enthalpies of the formation of ion pair **IV** by the ion generation reaction between **III** and BCl_3 are shown in Table 1.

The equilibrium interionic distance (the distance between the carbocationic carbon and boron atoms) calculated by the MNDO method for ion pair **IV** in vacuum is 4.13 Å. There are no other local minima of the potential energy surface in vacuum with ion pair-like geometry. To estimate the influence of the polar solvent on the interionic distance, which seems to be the only solvent-sensitive geometrical parameter of the ion pair, the following procedure was employed. The geometries of ion pair **IV** at fixed interionic distances in the range from 4.5 to 6.4 Å were completely optimized in vacuum using the EF minimization procedure. At

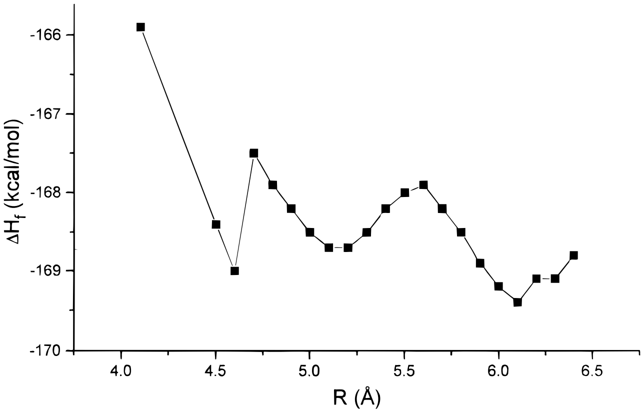


Figure 2. MNDO-calculated dependence of the ΔH_f value for ion pair **IV** on the interionic distance in a polar solvent with $\epsilon = 12$. All other geometrical parameters of the ion pair are completely optimized in vacuum at each value of the interionic distance.

these vacuum-optimized geometries with different interionic distances, the ΔH_f values in polar solvent were calculated. The dependence of the ΔH_f value, calculated at $\epsilon = 12$, on the interionic distance (R) is shown in Figure 2. As can be seen in this figure, there are three distinct ΔH_f minima at $R = 4.6$, 5.1−5.2, and 6.1 Å, with nearly equal ΔH_f values. The geometries of the three minima, together with the geometry of ion pair **IV** optimized in vacuum, are presented in Figure 3. As exhibited in this figure, the minima with different interionic distances differ by the orientation of the anion with respect to the carbocationic center. It should be noted that the calculated ΔH_f values for these minima can hardly be used for an estimation of the populations for each of the minima because of the rather approximate character of the semiempirical calculation procedure. It may only be expected that the true R value for the ion pair in polar solvent with $\epsilon = 12$ is in the range 4.6−6.1 Å.

Taking into account that the ΔH_f value for ion pair **IV** at solvent-optimized geometry is by ca. 3.5 kcal/mol lower than that for the vacuum-optimized geometry (Table 1), as one can see from Figure 2, the enthalpy of the reaction **III** + $BCl_3 \rightarrow$ **IV** in polar medium is as low as $\Delta H = 7.2$ kcal/mol, indicating that the formation of ion pair **IV** can occur in polar solvents.

Initiation of Polymerization. As found in earlier calculations,[8] a zwitterionic intermediate of type **I** is capable of addition of a monomer molecule, leading to a new zwitterionic structure, which can be considered as the initiation of IB polymerization. The reaction between **I** and IB leads to the formation of structure **V**:

$$\mathbf{I} + i\mathrm{C_4H_8} \rightarrow \mathrm{Cl_3B^{-}CH_2C(CH_3)_2CH_2C^{+}(CH_3)_2} \quad (\mathbf{V})$$

To compare the initiation reaction via the zwitterionic intermediate **I** with that by ion pair **IV**, the structure of a new ion pair formed by addition of IB to ion pair **IV** was also calculated:

$$\mathbf{IV} + i\mathrm{C_4H_8} \rightarrow \mathrm{Cl_2BCH_2C(CH_3)_2CH_2C^{+}(CH_3)_2/BCl_4^{-}} \quad (\mathbf{VI})$$

The completely optimized-vacuum geometries of structures **V** and **VI** are shown in Figure 4.

The ΔH_f values and the enthalpies of the formation of **V** from **I** and IB and of **VI** from **IV** and IB are presented in Table 1. These data indicate that the formation of **V** and **VI** is possible only in the polar medium due to nonspecific solvation of these strongly ionic species. In polar solvent ($\epsilon = 12$), the formation of structure **VI** by a reaction between IB and **IV** is thermoneutral according to the data of MNDO calculations ($\Delta H = 0$), whereas the reaction between IB and the zwitterionic intermediate **I** for obtaining **V** is quite endothermic ($\Delta H = 13.1$ kcal/mol). This indicates that initiation should occur by ion pairs of type **IV** rather than by zwitterionic structures of type **I** in BCl_3-induced LCCP of isobutylene. As widely used in the practice of polymerization studies, these initiation processes can be viewed as model reactions for further monomer addition steps, i.e., for propagation, leading to the formation of a polymer chain. This means that the data and conclusions obtained for the initiation step can be extended to propagation as well.

Propagation Enthalpies. According to experimental data,[13] the polymerization enthalpy of isobutylene is markedly negative ($\Delta H = -17.2$ kcal/mol). The propagation enthalpies of IB polymerization (ΔH_p) were calculated by the MNDO method for the following two reactions: (1) IB insertion into ion pair **IV** and (2) IB insertion into the C−Cl bond of the neutral species **III**. The results of these calculations are summarized in Tables 2 and 3. As exhibited in Table 3, for none of these reactions are the MNDO values of ΔH_p close to the experimental ΔH_p value. On the basis of experience with MNDO calculations, it seems to be quite obvious that this is due to the well-known MNDO tendency to overestimate the repulsion between chemically nonbonded atoms. In the present case, the overestimated repulsion should exist between the methyl groups of ultimate and penultimate IB units of a growing polymer chain. This effect could be checked by PM-3 calculations of the corresponding ΔH_p values, since the PM-3 method has overcome the above-mentioned MNDO defect to a considerable extent.[10] However, PM-3 parameters for boron are unavailable at the present time. Therefore, we calculated by the PM-3 method the ΔH_p values for IB insertion into the C−Cl bond, having replaced the Cl_2B endgroup with an H atom. The results are shown in Tables 2 and 3, together with the corresponding MNDO data. As can be seen in Table 3, in contrast to the MNDO method, the PM-3 method gives negative ΔH_p values, in good agreement with the experimental data.[13] The MNDO values of ΔH_p are 20−22 kcal/mol higher than the corresponding PM-3 values (see Table 3).

Ion Pair Dissociation Enthalpies. The enthalpies of dissociation (ΔH_d) of ion pairs into free ions can be calculated from the ΔH_f values for BCl_4^- (see Table 1) and the corresponding free cations (see Table 2). The ΔH_d values for ion pairs **IV**, **VI**, and $Cl_2B(CH_2C(CH_3)_2)_3^+/BCl_4^-$ are slightly negative in polar solvents if vacuum-optimized geometries of ion pairs are used for the nonspecific solvation energy calculations ($\Delta H_d = -1.8$, −0.6, and −0.7 kcal/mol, respectively). Accounting for the decrease in the energies of the ion pairs by ca. 3.5 kcal/mol due to a solvent-induced increase of the interionic distance (as estimations for ion pair **IV** discussed above show), the ΔH_d values are slightly positive (i.e., 1.7, 2.9, and 2.8 kcal/mol, respectively) but close to zero within the computational accuracy.

Conclusions

Two different mechanisms of initiation (and propagation) of LCCP of IB by BCl_3 in polar solvents have been

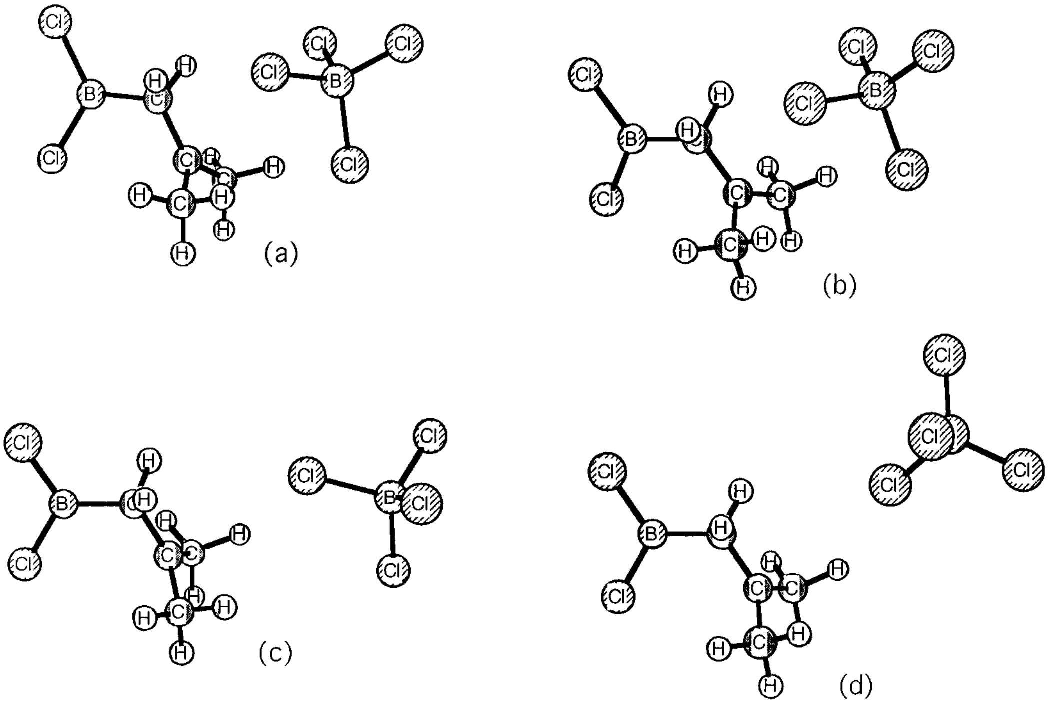


Figure 3. Completely optimized geometries of ion pair **IV**. The distance between the carbocationic center and the boron atom of the counteranion, *R*(C−B), and between carbocationic center and chlorine atoms of the counteranion, *R*(C−Cl). (a) $\epsilon = 1$; *R*(C−B) = 4.13 Å, *R*(C−Cl) = 3.85, 3.85, 3.86, 5.95 Å. (b) $\epsilon = 12$; *R*(C−B) = 4.6 Å, *R*(C−Cl) = 4.26, 4.26, 4.26, 6.42 Å. (c) $\epsilon = 12$; *R*(C−B) = 5.2 Å, *R*(C−Cl) = 3.71, 4.98, 6.33, 6.33 Å. (d) $\epsilon = 12$; *R*(C−B) = 6.1 Å, *R*(C−Cl) = 4.17, 6.86, 6.86, 6.90 Å.

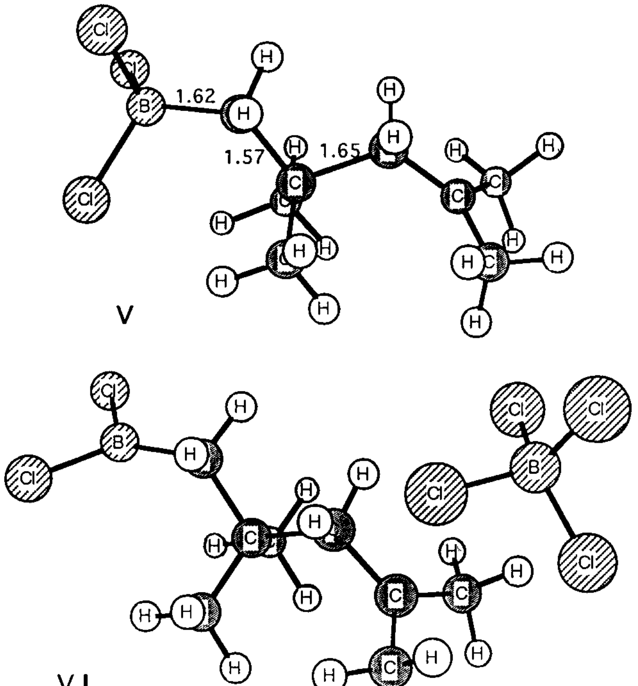


Figure 4. Completely optimized vacuum geometries of zwitterionic structure **V** and ion pair **VI**. For structure **VI**, the distance between the carbocationic center and the boron atom of the counteranion, *R*(C−B), and between the carbocationic center and the chlorine atoms of the counteranion, *R*(C−Cl), are *R*(C−B) = 4.17 Å, and *R*(C−Cl) = 3.88, 3.88, 3.95, and 6.00 Å.

investigated using the MNDO method. Scheme 1 summarizes the elementary processes and corresponding ΔH and ΔH_f values for initiations by direct chloroboration and by formation of zwitterionic structures with the involvement of two IB and two BCl_3 molecules. As

Table 2. MNDO and PM-3-Calculated Values of ΔH_f for Different Structures Used for the Calculations of ΔH_p and ΔH_d Values (See Table 1 for ΔH_f Values for Structures III, IV, and VI)

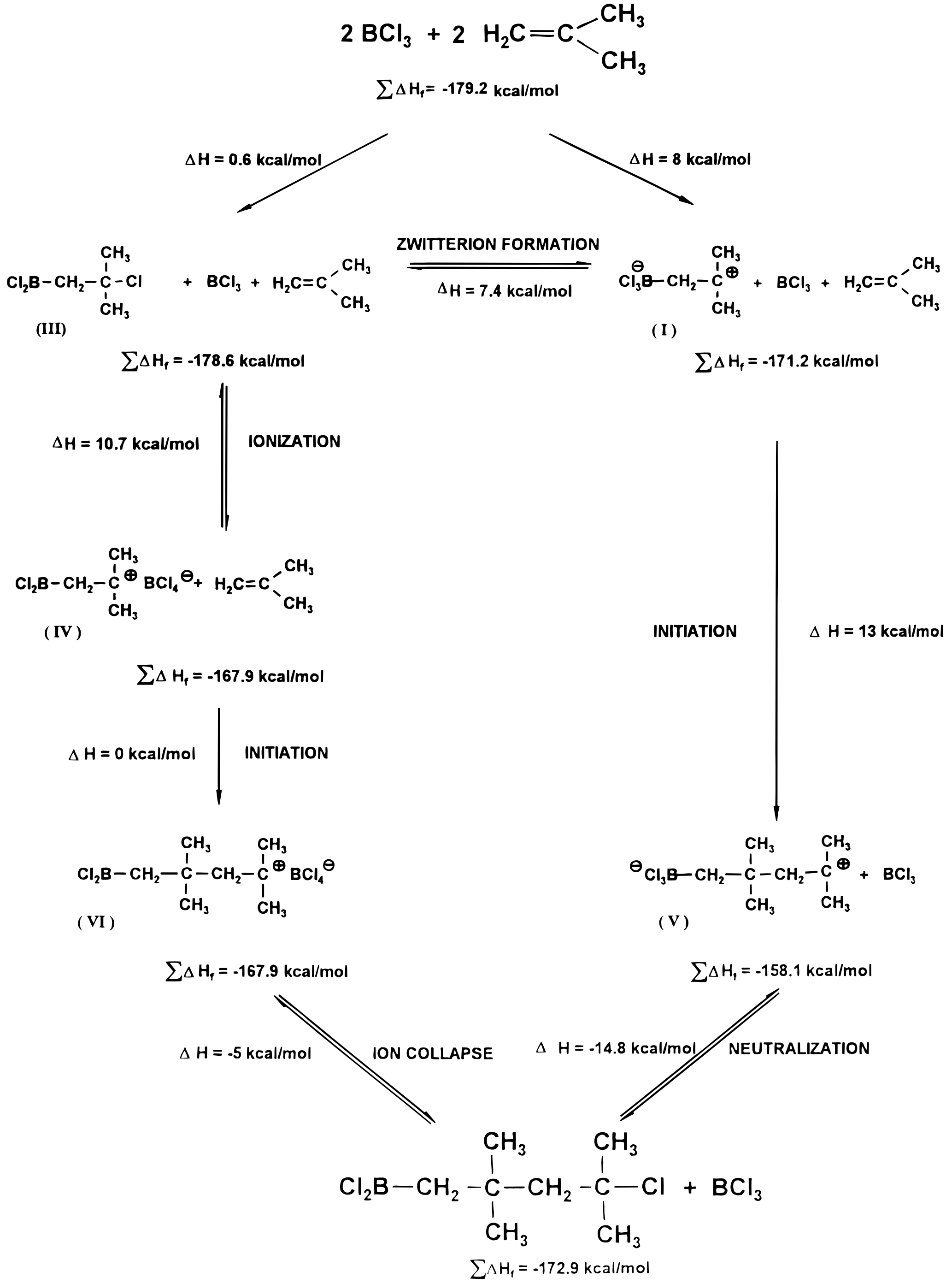
		ΔH_f (kcal/mol)	
structure	ϵ	MNDO	PM3
$Cl_2B(CH_2C(CH_3)_2)_3^+/BCl_4^-$	1	−134.1	
	12	−161.9	
$Cl_2B(CH_2C(CH_3)_2)_2Cl$	1	−82.9	
	12	−85.3	
$Cl_2B(CH_2C(CH_3)_2)_3Cl$	1	−75.9	
	12	−78.3	
$Cl_2BCH_2C(CH_3)_2^+$	1	131.6	
	12	78.7	
$Cl_2B(CH_2C(CH_3)_2)_2^+$	1	129.2	
	12	77.9	
$Cl_2B(CH_2C(CH_3)_2)_3^+$	1	133.7	
	12	83.8	
$HCH_2C(CH_3)_2Cl$	1	−31.7	−37.8
	12	−33.3	−38.3
$H(CH_2C(CH_3)_2)_2Cl$	1	−28.6	−55.9
	12	−30.1	−56.6
$H(CH_2C(CH_3)_2)_3Cl$	1	−21.5	−71.5
	12	−23.1	−72.2

shown in this scheme, the chloroboration reaction between IB and BCl_3 is almost thermoneutral, with a rather low energy barrier in a polar solvent, whereas the ΔH value is significantly higher for the formation of a zwitterionic structure (**I**). Initiation of LCCP of IB by an ion pair (**IV**), formed as a result of Cl^- abstraction from the product (**III**) of the chloroboration reaction by another BCl_3 molecule leading to **VI**, is more favorable than that by a zwitterionic intermediate (**I**) resulting in **V**. It should be noted here that, for the zwitterionic structure **V**, an *all-trans*, fully extended conformation was used (see Figure 4a). It can be suggested that folding of this conformation leading to the decrease in the distance between the oppositely charged ends of the structure **V** may stabilize this species. However, it was found that the energy of structure **V** hardly depends on its conformation in a polar solvent. The reason for this

Table 3. MNDO- and PM-3-Calculated Values of Propagation Enthalpies (ΔH_p) for Different Reactions (See Table 1 for ΔH_p of Reaction IV + IB → VI)

reaction	ϵ	ΔH_p (kcal/mol) MNDO	ΔH_p (kcal/mol) PM-3
VI + IB → $Cl_2B(CH_2C(CH_3)_2)_3{}^+/BCl_4{}^-$	1	7.3	
	12	8.0	
III + IB → $Cl_2B(CH_2C(CH_3)_2)_2Cl$	1	5.6	
	12	5.7	
$Cl_2B(CH_2C(CH_3)_2)_2Cl$ + IB → $Cl_2B(CH_2C(CH_3)_2)_3Cl$	1	8.8	
	12	9.0	
$HCH_2C(CH_3)_2Cl$ + IB → $H(CH_2C(CH_3)_2)_2Cl$	1	4.9	−15.3
	12	5.2	−15.0
$H(CH_2C(CH_3)_2)_2Cl$ + IB → $H(CH_2C(CH_3)_2)_3Cl$	1	8.9	−12.8
	12	9.0	−12.3

Scheme 1. Elementary Stages of the Initiation Process of LCCP of IB by Chloroboration and by Zwitterion (I) Formation with the Corresponding Thermodynamic Data Obtained by MNDO Calculations



is that two opposite effects compensate each other upon the transition from the extended to the folded conformation of **V**: (1) the decrease in energy due to the increasing Coulombic attraction of the oppositely charged ends and (2) the increase in energy due to the decreasing stabilization caused by the nonspecific solvation (the structure becomes less polar upon folding of the conformation).

The ΔH_f values for the reactions of ion collapse (neutralization) indicate that propagation of IB polymerization is more probable with ion pair **VI** than with the zwitterionic structure **V**, for which the neutralization (termination) is more favorable than that for **VI**. In other words, the thermodynamic characteristics of the initiation (and propagation) processes proceeding via ion pair formation suggest that these reactions may quite easily occur in polar solvents like CH_3Cl and CH_2Cl_2. Thus, the data obtained in this study are supportive of the direct chloroboration mechanism proposed on the basis of kinetic investigations of LCCP of IB in these polar solvents.[6,7] A strong stabilizing effect of the polar solvent on ion pairs in BCl_3-induced LCCP of IB has been also established. This is in agreement with experimental findings, according to which BCl_3 is relatively ineffective to induce LCCP of IB in nonpolar solvents and polar/nonpolar solvent mixtures.[12] The interionic distance in the ion pairs calculated by the MNDO method is rather sensitive to the polar solvent environment. The results of calculations suggest that several ion pair structures of type **IV** may exist, with different interionic distances in the range from 4.6 to 6.1 Å in polar solvents.

In Scheme 1, the MNDO method provides somewhat positive ΔH_p. As discussed earlier in this article, the MNDO method overestimates the repulsion between nonbonded atoms, but the data obtained with this method are useful for comparison between the relative energetics of different reactions. One can obtain ΔH_p values near to experimental findings by the PM-3 method. However, carrying out PM-3 calculations for the reactions discussed is limited due to the lack of PM-3 parameters for the boron atom.

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Supporting Information Available: MNDO and PM-3 output files containing detailed information about the geometries and energies of the studied compounds (10 pages). See any current masthead page for ordering information.

References and Notes

(1) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser Publishers: Munich, 1992.
(2) Iván, B.; Kennedy, J. P. *Ind. J. Technol.* **1993**, *31*, 183.
(3) Iván, B. *Makromol. Chem., Macromol. Symp.* **1993**, *75*, 181.
(4) Gandini, A. In *Comprehensive Polymer Science*, 1st Suppl.; Allen, G., Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: Oxford, 1992; pp 107.
(5) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.
(6) Balogh, L.; Wang, L.; Faust, R. *Macromolecules* **1994**, *27*, 3453.
(7) Balogh, L.; Fodor, Zs.; Kelen, T.; Faust, R. *Macromolecules* **1994**, *27*, 4648.
(8) Yakimansky, A. V.; Erussalimsky, B. L.; Zubkov, V. A. *J. Macromol. Sci.-Pure Appl. Chem.* **1994**, *A31*, 261.
(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(10) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
(11) Chudinov, G. E.; Napolov, D. V.; Basilevsky, M. V. *Chem. Phys.* **1992**, *160*, 41.
(12) Iván, B.; Kennedy, J. P. *Macromolecules* **1990**, *23*, 2880.
(13) Parks, G. S.; Mosher, H. P. *J. Polym. Sci.* **1963**, *A1*, 1979.

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