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# QUANTUM CHEMICAL STUDY OF THE MECHANISM OF THE LIVING CATIONIC POLYMERIZATION BY ESTER-BORON TRIHALIDE INITIATORS

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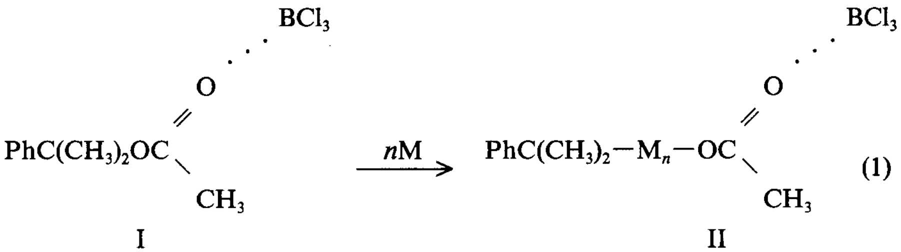
## ABSTRACT

Semiempirical MNDO calculations of model systems simulating cationic initiating systems of the $BCl_3$/ester type have been carried out. Interactions between $BX_3$ ($X = F, Cl$) and methyl acetate (MA) have been compared. Properties of six-membered cyclic transition states for the reaction between MA and propylene in the presence of $BCl_3$, previously proposed as a mechanism of living cationic polymerization, have been investigated. An alternative mechanism of polymerization via zwitterionic complexes formed between $BCl_3$ and monomer has been suggested. The cationic center of this zwitterionic complex has been found to be stabilized by the ester component of the initiating system.

## INTRODUCTION

In recent years Kennedy and coworkers have developed a number of new cationic initiating systems which provide for the effective polymerization of several monomers without chain termination and transfer reactions. The results of these studies are summarized in Ref. 1 (see also a review [2]).

One of the above-mentioned systems is a combination of $BCl_3$ with esters of the general structure $PhC(CH_3)_2OCOR$. At first sight the active sites (AS) formed in these systems could be considered as ionic pairs corresponding to common binary cationic systems on the basis of Lewis acids. In that case, the initial AS should have the structure $[PhC(CH_3)_2]^+[BCl_3OCOR]^-$. However, a number of peculiarities of the polymerization processes studied (for example, the living character of polymerization in these processes) could not be explained if the AS had the above ionic pair structure. Therefore, another structure for the initial AS and the corresponding mechanism of its interaction with the monomer can be described as follows [taking cumyl acetate (CA) as an example]:

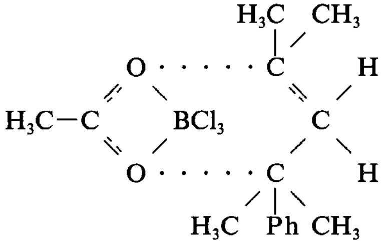


I

II

(1)

According to Plesch [3], the insertion of a monomer molecule (for example, isobutene) into the C—O bond of an ester proceeds via a six-membered transition state (TS), with the $BCl_3$ molecule being simultaneously transferred from its original site to the new carbonyl oxygen:

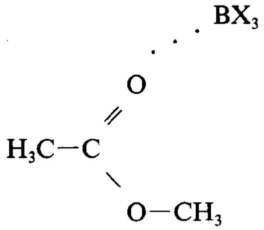


III

Experimental data are in agreement with Reaction (1) proceeding via this TS [3]. It seems useful to calculate the structural and electronic characteristics of AS of Type I and TS of Type III.

## SUBJECTS AND METHODS OF CALCULATION

In this study, semiempirical MNDO [4] calculations of the model AS involving methyl acetate (MA) and $BX_3$ (X = F, Cl) were carried out.



IV

An analysis of different possible ways of monomer molecule (propylene) interaction with this AS and its components, including the mechanism of the type

I→III→II suggested by Plesch [3], was also performed. Investigation of systems with different halide atoms X was carried out in order to explain the advantages of $BCl_3$ in comparison to $BF_3$, which is frequently used in the initiating systems of the $BF_3$-ether type [5]. For our calculations, the AMPAC program [6] using the MNDO algorithm was employed. Geometry optimization was carried out by the Fletcher-Powell method [7] for the ground states of molecules and by minimization of the gradient norm [8] for TS. All TS obtained are characterized by only one imaginary vibrational eigenvalue of the Hessian matrix.

It should be noted that solvent effects were not included in our calculations. As discussed below, these effects may be estimated qualitatively by a comparison of the dipole moments of the initial reagents and the TS of the reactions. It was shown that these qualitative predictions for the proposed mechanism are in agreement with the experimental data.

## RESULTS AND DISCUSSION

The equilibrium geometries of Complexes IV are shown in Figs. 1(a) and 1(b). In Table 1 the heats of formation $\Delta H_f$, atomic charges $q$, bond orders $p$, and dipole moments $\mu$ for Complexes IV and their components are given. The interaction energies $\Delta E$ of the ester and Lewis acid (computed as the difference between the $\Delta H_f$ value of the complex and the sum of the $\Delta H_f$ values of the ester and the $BX_3$

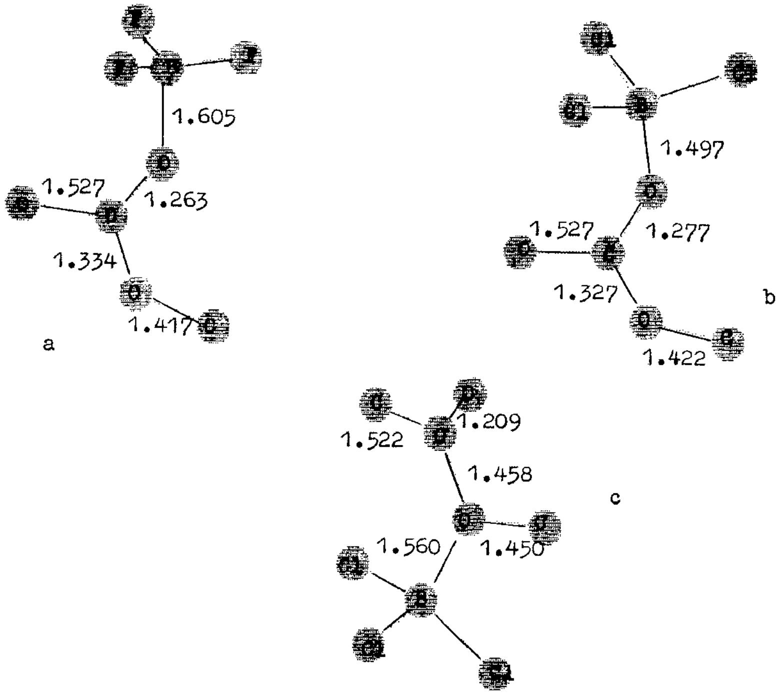
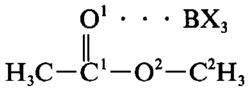


FIG. 1.

TABLE 1. Characteristics of the Complexes



$$\begin{array}{c} O^1 \cdots BX_3 \\ \| \\ H_3C{-}C^1{-}O^2{-}C^2H_3 \end{array}$$

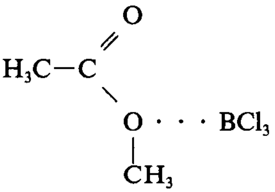
and Their Components (methyl acetate and $BX_3$, X = F, Cl)

| | Structure | | | | |
|---|---|---|---|---|---|
| Characteristics | $BF_3$/methyl acetate | $BCl_3$/methyl acetate | Methyl acetate | $BF_3$ | $BCl_3$ |
| $\Delta H_f$, kJ/mol | −1457.7 | −776.9 | −368.6 | −1090.9 | −365.5 |
| Atomic charges, $q$: | | | | | |
| $C^1$ | 0.4792 | 0.4900 | 0.3314 | — | — |
| $O^1$ | −0.3085 | −0.2341 | −0.3078 | — | — |
| $O^2$ | −0.3003 | −0.2799 | −0.3314 | — | — |
| B | 0.4372 | 0.1833 | — | 0.5270 | 0.1801 |
| Bond orders, $p$: | | | | | |
| $C^1{=}O^1$ | 1.5396 | 1.4491 | 1.8742 | — | — |
| $C^1{-}O^2$ | 1.1464 | 1.1931 | 0.9776 | — | — |
| $O^2{-}C^2$ | 0.8897 | 0.8790 | 0.9485 | — | — |
| $O^1{-}B$ | 0.4942 | 0.7033 | — | — | — |
| Dipole moment, $\mu$, D | 7.894 | 9.709 | 4.110 | 0.0 | 0.0 |
| Interaction energy $\Delta E$ of the complex components, kJ/mol | 1.7 | −42.8 | — | — | — |
| Total charge of $BX_3$ | −0.3632 | −0.5071 | — | 0.0 | 0.0 |
| Energy of LUMO, eV | — | — | — | 1.197 | −1.905 |

molecule), the total charge values of the Lewis acid molecule for Complexes IV, and the energies of the lowest unoccupied molecular orbital (LUMO) for the $BX_3$ molecules are also presented.

As seen in Table 1, the $\Delta E$ value is positive for X = F and negative for X = Cl. Thus, at the equilibrium geometry of the complex there is repulsion between $BF_3$ and the ester and attraction between $BCl_3$ and the ester. This correlates with the positive value of the LUMO for $BF_3$ and the negative value of LUMO for $BCl_3$ (see Table 1). These results are in agreement with the experimental fact that $BCl_3$ is a stronger Lewis acid than is $BF_3$ [9] and with the data of ab-initio calculations [10, 11].

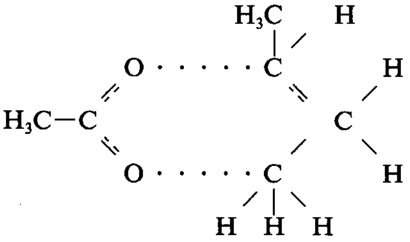
It is worthwhile to note that although the negative charge of the etherlike oxygen of methyl acetate is higher than that of the carbonyl oxygen (see Table 1), the bonding of an ester to the Lewis acid is most effective at the carbonyl oxygen atom. The calculation carried out for the Complex V showed that its energy is ~115.0 kJ/mol higher ($\Delta H_f = -661.9$ kJ/mol) than that for Complex IV. The explanation is that contributions of atomic orbitals of the etherlike oxygen of methyl acetate into the highest occupied molecular orbital (HOMO), interacting with the LUMO of $BCl_3$, are lower than those of the atomic orbitals of the carbonyl oxygen.



V

The equilibrium geometry of Complex V is shown in Fig. 1(c). The equilibrium value of the O · · · B distance for Complex V is 1.56 Å. The similar complex with $BF_3$ instead of $BCl_3$ does not exist (the equilibrium O · · · B distance is higher than 4 Å). Therefore, the complex of Type V cannot be the AS of cationic polymerization despite its O—C bond being weaker ($p = 0.8288$) than that of Complex IV ($p = 0.8790$, see Table 1).

An increase in attraction between the components of Complexes IV in the series X = F, Cl correlates (as seen from Table 1) with the decrease in O · · · B distance and the increase of electron density transfer from ester to $BX_3$. Moreover, the C=O and O—C bonds are weaker in the case X = Cl compared to those in the case X = F. The weakening of the O—C bond may cause a decrease in the activation energy of monomer insertion into this bond as it occurs in Eq. (1). In order to check this suggestion, we analyzed the properties of the TS for the reaction of MA with propylene in the absence of Lewis acid and in the presence of $BCl_3$ with different initial positions of the $BCl_3$ molecule with respect to a cyclic TS of Type VI.



VI

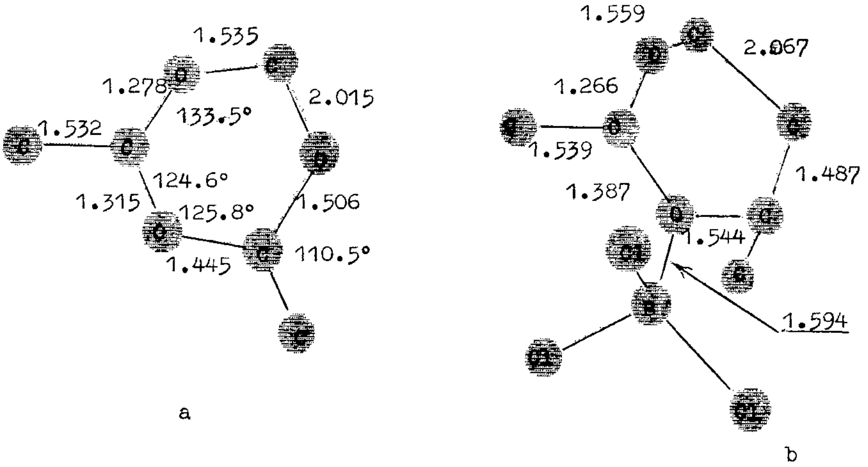


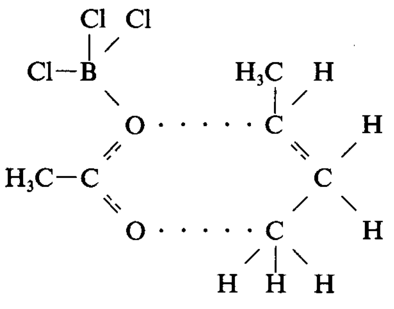
FIG. 2.

The geometry of TS VI is shown in Fig. 2(a). Its $\Delta H_f$ value, atomic charges, and bond orders are presented in Table 2.

It should be noted that the activation energy $\Delta E\ddagger$ of propylene insertion into the C—O bond of methyl acetate is rather high [$\Delta E\ddagger = \Delta H_f(\text{VI}) - \Delta H_f(\text{MA}) - \Delta H_f(\text{propylene}) = 448.3$ kJ/mol; $\Delta H_f$(propylene) is equal to 21.6 kJ/mol]. This is not surprising because the TS VI is similar to the TS of ester pyrolysis reactions which are known to proceed slowly at elevated temperatures [12].

It can be seen from the geometry (Fig. 2a) and bond orders (Table 2) that both oxygen atoms in TS VI are etherlike because the bond between the original carbonyl oxygen and monomer molecule is almost completely formed and the bond between the new carbonyl oxygen and the $CH_3$ group is still rather strong and only ~10% longer compared to the equilibrium value of the O—$CH_3$ bond in methyl acetate (1.398 Å). Taking this into account, one can hardly expect a strong stabilization of the cyclic TS by $BCl_3$ interaction with both oxygens, because $BCl_3$ is strongly repelled from the etherlike oxygen of MA in Complex V. Moreover, it is seen from Table 2 that the carbon atom of the $CH_2$ group of the propylene moiety has the highest negative charge. Therefore, the HOMO of TS VI is almost completely centered at this atom. However, it is impossible for $BCl_3$ to interact with the $CH_2$ group without destruction of the six-membered cyclic TS fragment.

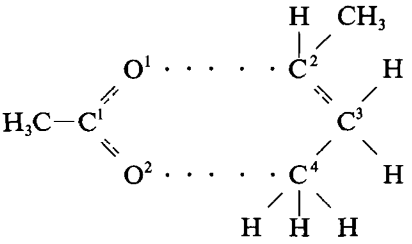
Indeed, our attempts to find a saddle point of the potential energy surface of the $BCl_3$-cyclic TS VI system with an energy lower than the sum of the energies of $BCl_3$ and TS VI were unsuccessful. When initially placed at the new carbonyl oxygen or above and between the two oxygen atoms of VI (such as in Structure III), the $BCl_3$ molecule is repelled from the cyclic TS fragment to distances greater than 4 Å. For the $BCl_3$ molecule position near the original carbonyl oxygen, the TS of Type VII was found to have $\Delta H_f = -97.3$ kJ/mol, exceeding the sum of the $\Delta H_f$ values for $BCl_3$ and the cyclic TS VI by more than 160 kJ/mol (the geometry of TS VII is shown in Fig. 2b).



VII

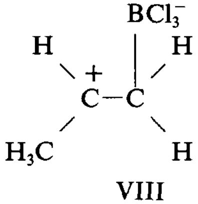
This result means that $BCl_3$ cannot be a catalyst for monomer insertion into the C—O bond of an ester. Therefore, the mechanism of polymerization via cyclic TS of Types III or VII does not agree with quantum chemical data. Moreover, the dipole moment of TS VII is 6.8 D, which is lower than that of Complex IV (9.7 D). Therefore, this TS is less polar than the initial reagents (Complex IV and propylene) and the polymerization rate constant via this TS should decrease with an increase in solvent polarity, which is in disagreement with experimental data [3].

TABLE 2. Characteristics of TS VI



| Characteristic | Value |
|---|---|
| $\Delta H_f$, kJ/mol | 101.3 |
| Atomic charges, $q$: | |
| $C^1$ | 0.4293 |
| $O^1$ | −0.2748 |
| $O^2$ | −0.2898 |
| $C^2$ | 0.1918 |
| $C^3$ | −0.4938 |
| $C^4$ | 0.4190 |
| Bond orders, $p$: | |
| $C^1{=}O^1$ | 1.2297 |
| $C^1{=}O^2$ | 1.4311 |
| $O^1{-}{-}C^2$ | 0.8241 |
| $O^2{-}{-}C^4$ | 0.5752 |
| $C^2{=}C^3$ | 0.9912 |
| $C^3{-}{-}C^4$ | 0.4155 |
| Dipole moment, $\mu$, D | 3.999 |

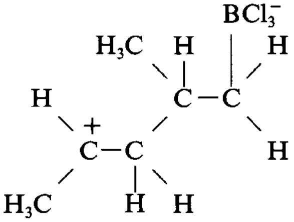
Looking for other possibilities, we found out that propylene forms a stable (i.e., corresponding to a local minimum of the potential energy surface) complex with $BCl_3$ of a zwitterionic nature:



VIII

This result does not seem to be an artifact of the MNDO method because usually MNDO does not predict stable zwitterionic structures. For example, both MNDO and ab-initio methods predict that zwitterionic adducts of amines to carbonyl compounds are not local minima of a potential energy surface and, therefore, are unstable [13].

Complex VIII appeared to be capable of adding a second monomer molecule and forming a new AS at the end of the growing chain because, as calculation showed, Structure IX is also stable:



IX

Equilibrium geometries of Species VIII and IX are shown in Figs. 3(a) and 3(b), and their $\Delta H_f$ values and some electronic characteristics are presented in Table 3. It is seen from Table 3 that Structures VIII and IX have very high dipole moments which explain the experimental increase in the polymerization rate constant with an increase in solvent polarity [3].

It is of interest that the complex similar to VIII with $BF_3$ instead of $BCl_3$ is unstable. The $BF_3$ molecule is repelled from the monomer to distances larger than 4 Å during geometry optimization. This fact is in agreement with the inability of $BF_3$ and complexes of $BF_3$ with ethers to initiate cationic polymerization unless traces of water are present in the initiating system [14].

The proposed mechanism of polymerization via the zwitterionic adduct of $BCl_3$ and the monomer molecule is similar to that proposed for the polymerization of 3-substituted indenes by $TiCl_4$ [15]. It has been shown by UV and $^{13}C$-NMR spectroscopies that $TiCl_4$ and indene form a zwitterionic adduct; its carbocationic center is capable of propagating polymerization [15].

In our opinion the role of the ester component of the initiating system $BCl_3$/ester could be to reduce the carbocation reactivity at the end of the growing chain that is necessary in order to protect the carbocationic AS from various deactivation reactions (e.g., chain termination by $Cl^-$ transfer from the $-BCl_3^-$ fragment of VIII to its carbocationic center, chain transfer, etc.). These reactions should prevent the

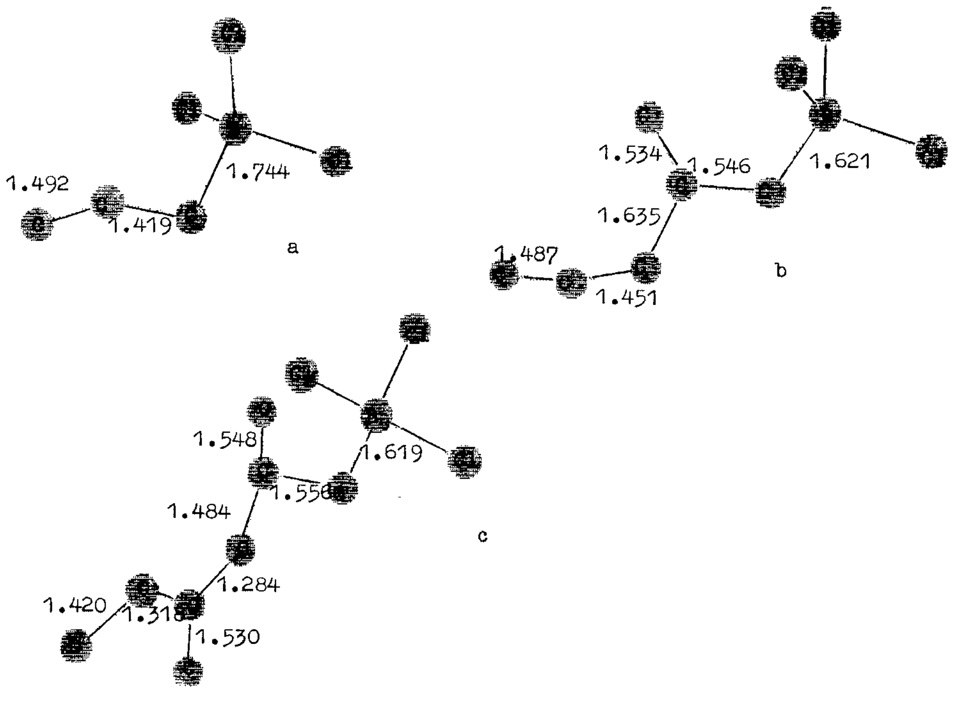
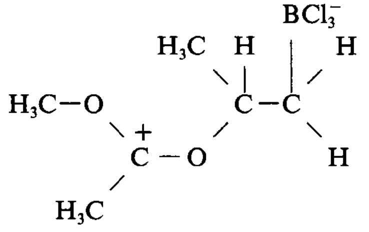


FIG. 3.

formation of long polymer chains in the $BCl_3$/monomer system without an ester or another Lewis base [16]. Calculations showed the possibility of stabilizing the carbocationic AS in VIII by binding it to the ester. In fact, MA forms a stable adduct with Complex VIII:

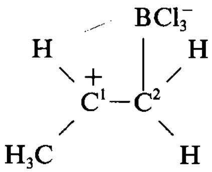
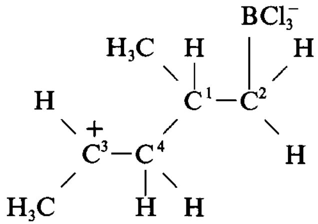
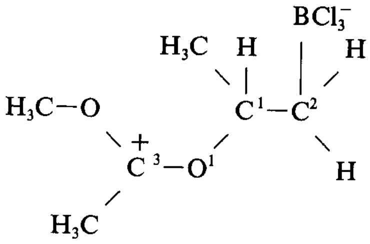


X

The equilibrium geometry of Adduct X is shown in Fig. 3(c), and its $\Delta H_f$ value and electronic characteristics are presented in Table 3. Calculations showed that this complex is unable to form a stable adduct with the second propylene molecule (propylene is repelled from the ester carbon of X during the geometry optimization). Therefore, adduct X cannot be an AS of polymer chain growth.

It is clear from the data of Table 3 that the formation of Adduct X from Complex VIII and MA is a nearly thermoneutral reaction ($\Delta H_f$(X) − $\Delta H_f$(VIII) − $\Delta H_f$(MA) = −4.5 kJ/mol), and that the formations of VIII from $BCl_3$ and propylene and of IX from VIII and propylene are endothermic processes ($\Delta H_f$-

TABLE 3. Characteristics of the Structures VIII, IX, and X

| Characteristic | Structure | | |
|---|---|---|---|
| |  VIII |  IX |  X |
| $\Delta H_f$, kJ/mol | −250.4 | −126.5 | −623.4 |
| Atomic charges, *q*: | | | |
| $C^1$ | 0.2969 | 0.0495 | 0.1620 |
| $C^2$ | −0.1520 | −0.0001 | −0.0126 |
| B | 0.1191 | 0.0861 | 0.0819 |
| $C^3$ | – | 0.3673 | 0.4644 |
| $C^4$ | – | −0.1434 | – |
| $O^1$ | – | – | −0.2144 |
| Bond orders, *p*: | | | |
| $C^1—C^2$ | 1.3588 | 0.9570 | 0.9458 |
| $C^2—B$ | 0.5981 | 0.8870 | 0.9002 |
| $C^1—C^4$ | – | 0.7673 | – |
| $C^1—O^1$ | – | – | 0.7310 |
| $C^3—C^4$ | – | 1.1842 | – |
| $C^3—O^1$ | – | – | 1.4466 |
| Dipole moment, $\mu$, D | 9.238 | 22.488 | 22.520 |

(VIII) − $\Delta H_f$(BCl$_3$) − $\Delta H_f$(propylene) = 93.6 kJ/mol and $\Delta H_f$(IX) − $\Delta H_f$(VIII) − $\Delta H_f$(propylene) = 102.2 kJ/mol). We believe that this fact is important due to the following reasons. MA should block up the carbocation center reversibly, because in the opposite case the reaction of MA with carbocation would be chain termination. This reversibility is provided by the thermoneutrality of MA addition to the carbocation. On the other hand, the monomer can successfully compete with the ester for the carbocationic centers in VIII or IX despite the endothermic character of the monomer addition to VIII which is due to the much higher concentration of the monomer in reaction volume as compared to that of the ester. If the monomer addition to species of Type VIII were an exothermic process, then the ester simply would not have a chance to react with the carbocation center and the polymerization would not possess features characteristic of a living process.

## CONCLUSIONS

The quantum chemical data presented make it possible to draw the following conclusions. First, calculation of interactions between MA and BX$_3$ confirms that BCl$_3$ is a stronger Lewis acid than BF$_3$. Second, the bonding of Lewis acid to ester is more favorable at the carbonyl oxygen atom than at the etherlike one. Third, the six-membered cyclic TS of the reaction between ester and monomer is characterized by a high activation energy. BCl$_3$ fails to polarize the C—O $\sigma$-bond of the ester significantly, which could have led to lowering of the energy of the six-membered cyclic TS and easier insertion of a monomer into this bond. Thus, according to the presented data, the previously proposed polymerization process mechanism initiated by the BCl$_3$/ester system [3] has to be reconsidered.

Calculations showed that the $\pi$-bond of the monomer is readily polarized by BCl$_3$, leading to the formation of stable zwitterionic complexes. Taking into account the higher polarizability of $\pi$-electrons as compared with that of $\sigma$-electrons, this result seems to be justifiable. The ability of zwitterionic complexes of BCl$_3$ with monomer to form stable adducts with another monomer molecule makes it possible to consider these zwitterionic complexes as AS of cationic polymerization. In this case the ester component of the initiating system serves as a stabilizer of the cationic centers of zwitterionic species.

It should be noted that the mechanism of living cationic polymerization proposed above may be generalized to other initiating systems providing a living character of cationic polymerization. For example, a living polymerization induced by initiating systems TiCl$_4$/2-Cl-2,4,4-trimethyl pentane containing various electron donors (esters, ethers, amides, pyridine, etc.) has been observed [17]. It seems that carbocations formed as a result of Cl$^-$ abstraction from alkyl chloride by TiCl$_4$ or by direct TiCl$_4$ interaction with monomer are stabilized against chain termination and transfer reactions by electron donors. An inhibition of polymerization in the presence of an excess of electron donor with respect to TiCl$_4$ [17] may be related to the absence of the free TiCl$_4$ necessary for the initiation reaction.

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