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ACTIVATION ENERGY AND THERMAL EFFECT OF INITIATION REACTION CATIONIC POLYMERIZATION OF *p*-METHYLSTYRENE IN THE PRESENCE OF COMPLEX CATALYSTS: BORON FLUORIDE - HYDROGEN FLUORIDE AND BORON FLUORIDE - WATER IN TOLUENE

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Abstract: This paper presents data on activation energy and thermal effects at the initiation stage of cationic polymerization of *p* -methylstyrene in the presence of complex catalysts: boron fluoride - hydrogen fluoride and boron fluoride – water in toluene having various stoichiometric composition. We studied the systems with following stoichiometric compositions BF_3-HF (H_2O) - *p*-methylstyrene-toluene, respectively: 1: 1: 1 (in the absence of toluene), 1: 1: 1: 1; 1: 1: 1: 2; 1: 1: 1: 3 and 1: 1: 1: 4, by quantum chemical calculation using the *ab ininto* method. It was shown that for BF_3-HF- *p*-methylstyrene - toluene system (I), the studied stoichiometric composition does not affect the activation energy of initiation. For BF_3-H_2O - *p*-methylstyrene - toluene system (II) system was established, that with toluene amount increase in this system the activation energy decreases.

Keywords*:* *p*-methylstyrene, protonation, boron fluoride - hydrogen fluoride catalyst, thermal effect of reaction, *ab initio* method.

Introduction

It is well known that toluene is an indifferent solvent widely used in various chemical reactions and, in particular, in the cationic polymerization reaction of various olefins [1]. Within traditional meaning the indifferent solvents are solvents whose interaction energy of molecules with a dissolved substance is no less than an order of magnitude lower than the solvation energy [2]. In this regard, often, especially when studying (modeling) the mechanisms of various chemical reactions, the influence of indifferent solvents was practically not taken into account and equated to the same reactions, but which take place in vacuum or in the absence of a solvent (for example see [3]). Nevertheless, it has already been noted that in indifferent solvent the reaction rates often differ from the rates that occur in the absence of solvents [4].

In this regard, the following tasks were set: 1) to ferret out the influence of indifferent solvent on mechanism and energetics of reaction, 2) to determine the thermal effects and activation barriers in initiation reaction of cationic polymerization of *p*-methylstyrene in the presence of complex catalysts BF_3-HF and BF_3-H_2O in toluene depending on amount of toluene. For this, we studied the systems BF_3-HF- *p*-methylstyrene-toluene (I) and BF_3-H_2O-*p*-methylstyrene-toluene (II) with following stoichiometric composition - 1(BF_3):1 (HF or H_2O): 1(*p*-methylstyrene):1 (toluene), 1:1:1:2, 1:1:1:3, 1:1:1:4.

It is advisable to theoretically estimate the values of activation barriers and thermal effects by quantum chemical calculation of studied initiation mechanisms of cationic polymerization for *p*-methylstyrene due to the fact that experimental methods can be very difficult (and often impossible) to determine the activation energy

Methodical part

To study the initiation mechanism of cationic polymerization for *p*-methylstyrene in the presence of above complex catalysts, the classical quantum-chemical *ab initio* method in the 6-311G** basis [5-6] was chosen as one of the best methods for estimating the activation energies and thermal effects of studied reactions [7-8]. When modeling of processes, the MacMolPlt program [9] was also used.

The initiation mechanism was studied in one coordinate (similarly to [10-12]). As the reaction coordinate for models (I) and (II) the $R_{C(1)–H(20)}$ bond was chosen. Multiplicity M = 1, because M = 2S + 1, where S is the resultant spin equal to 0 due to the fact that all electrons are paired. Throughout the interaction path of catalyst and *p*-methylstyrene and at each stage, the charge conservation law was fulfilled, i.e. the distributed total charge on all atoms is zero. The simulation was carried out in accordance with Markovnikov rule, i.e. the proton attacks the most hydrogenated carbon atom of *p*-methylstyrene - C(1).

Calculation data

The initial models (I) and (II) with stoichiometric composition 1:1:1:1 are presented in Fig. 1 and 5, and final structures (after the interaction of catalyst with a monomer) are shown in Fig. 2 and 6. Changes in total system energy along the reaction coordinate R are shown in Fig. 3 and Fig.7, and changes in charges at the atoms - in Fig. 4 and Fig 8. The values of activation energies and thermal effects for different stoichiometric composition of components are presented in Table 1 and Table 2.

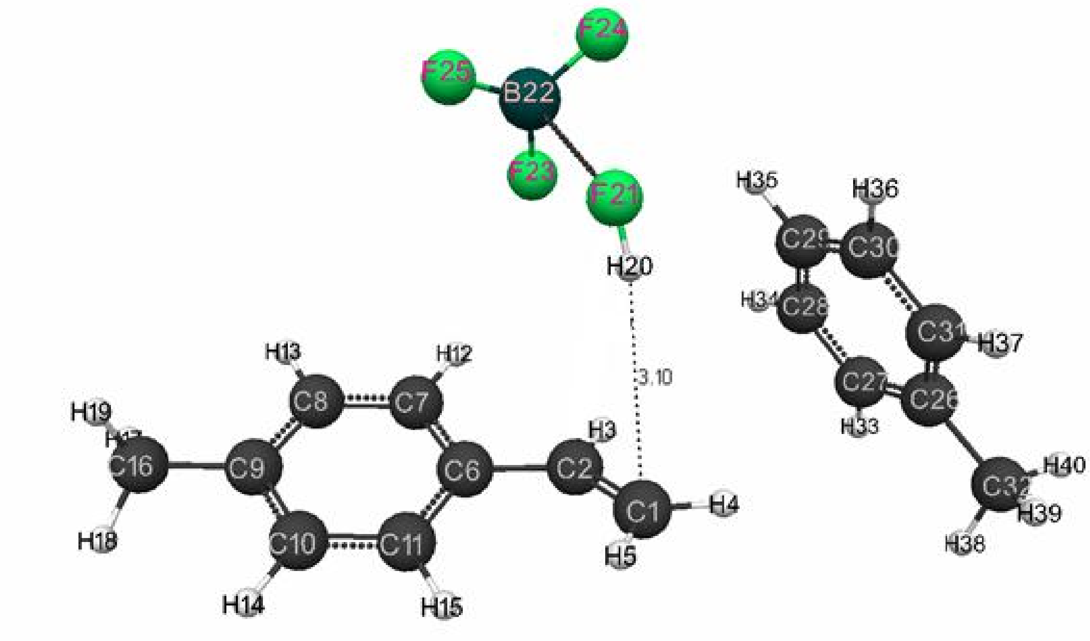

Figure 1. *Structure of original model (I) of complex catalyst HF·BF*$_3$ *with p-methylstyrene in toluene having stoichiometric composition 1:1:1:1.*

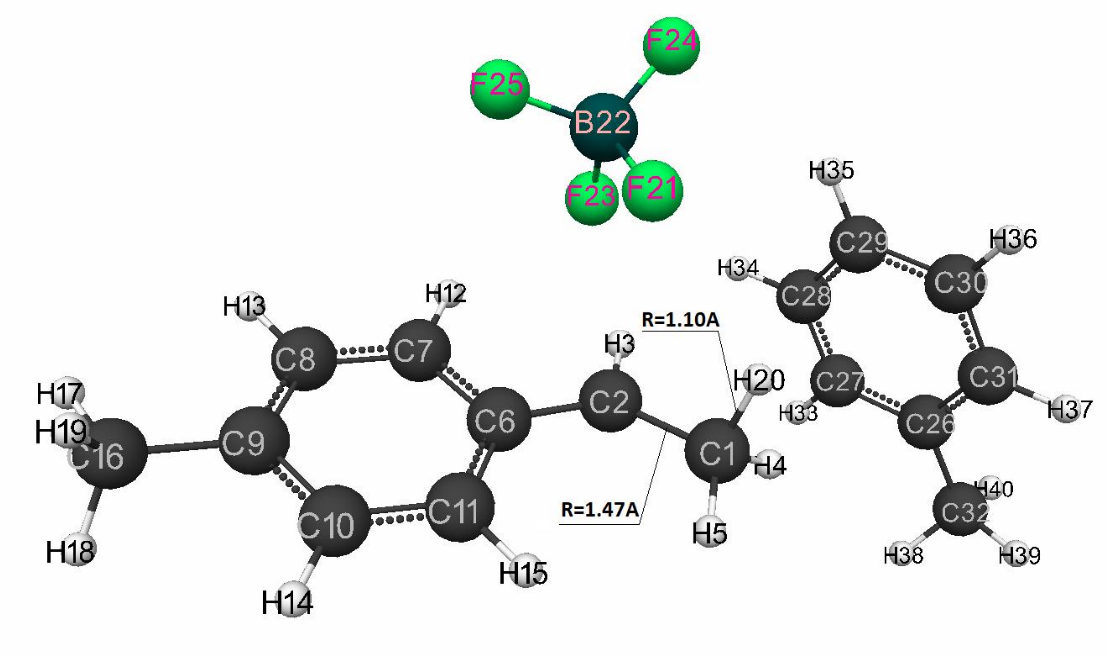

Figure 2. *Final structure of complex catalyst HF·BF$_3$ interaction with p-methylstyrene in toluene having stoichiometric composition 1:1:1:1.*

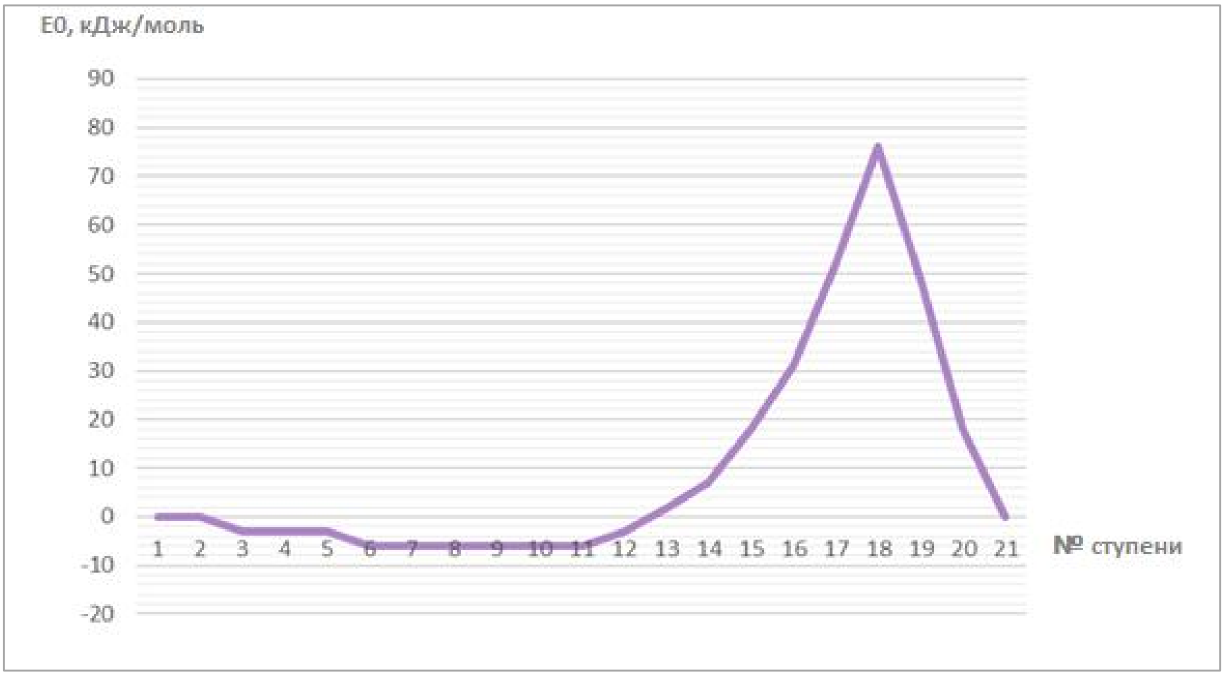

Figure 3. *Change in total energy (E$_0$) of studied reaction (1st -21th stages of interaction).*

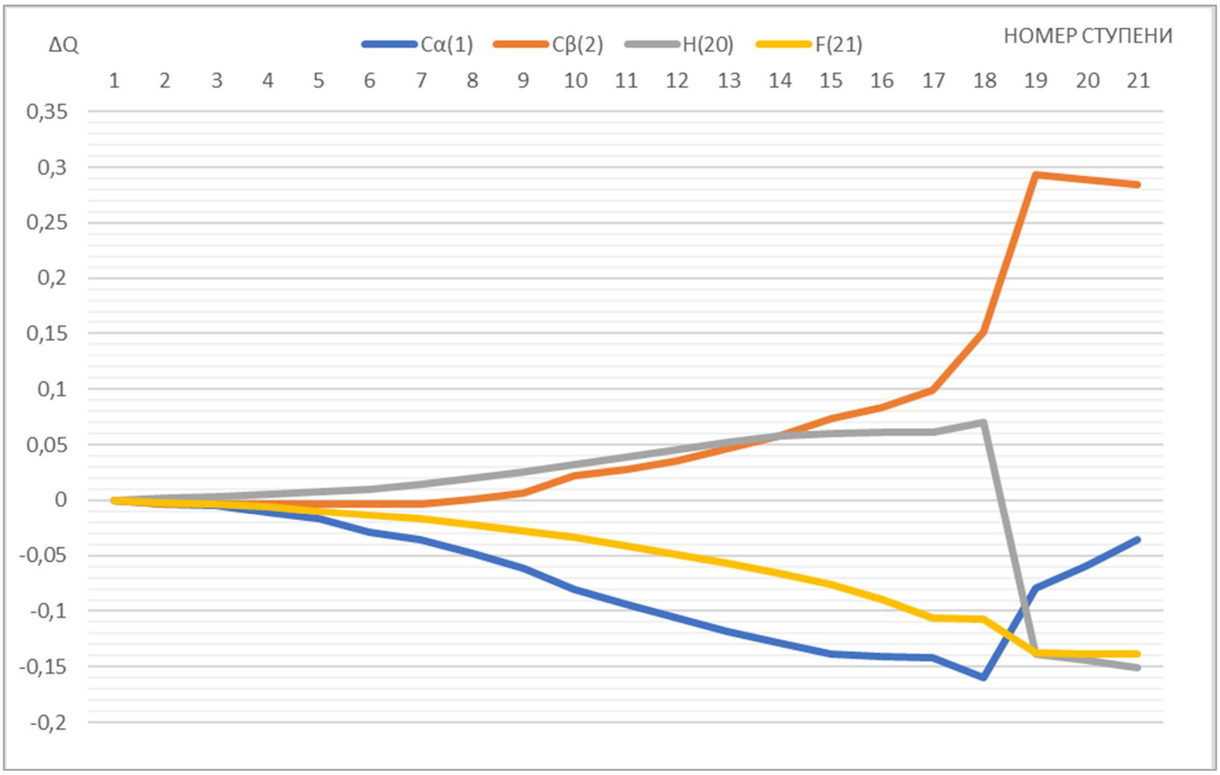

Figure 4. *Change of charges along reaction coordinate in system (I) having stoichiometric composition 1:1:1:1.*

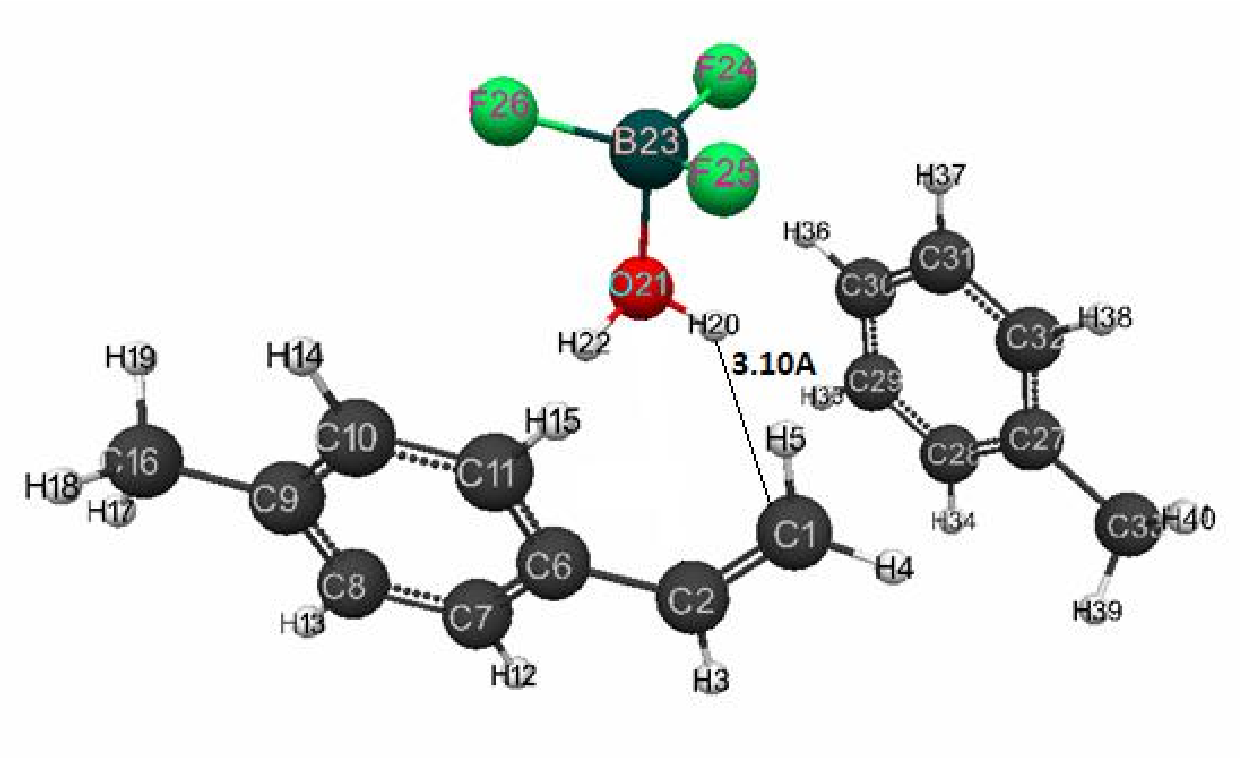

Figure 5. *Initial model structure of complex catalyst $H_2O{\cdot}BF_3$ with p-methylstyrene in toluene having stoichiometric composition 1:1:1:1.*

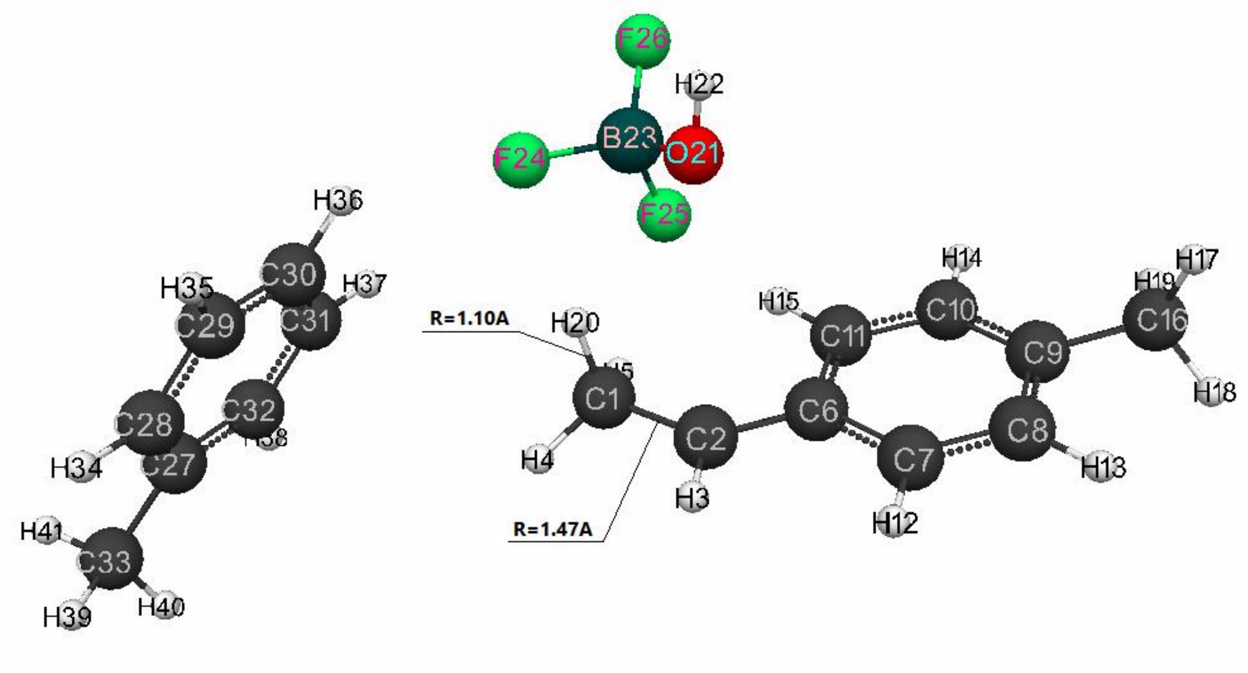

Figure 6. *Final interaction structure of complex catalyst $H_2O{\cdot}BF_3$ with p-methylstyrene in toluene having stoichiometric composition 1:1:1:1.*

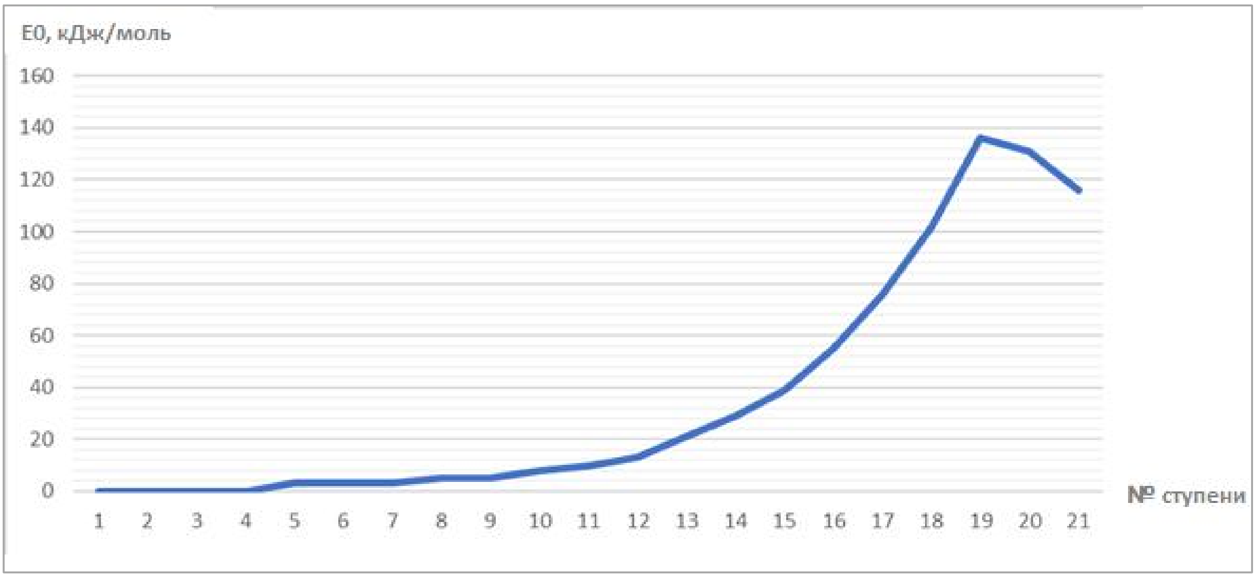

Figure 7. *Change in total energy (E_0) of studied reaction (1st -21th-stages of interaction).*

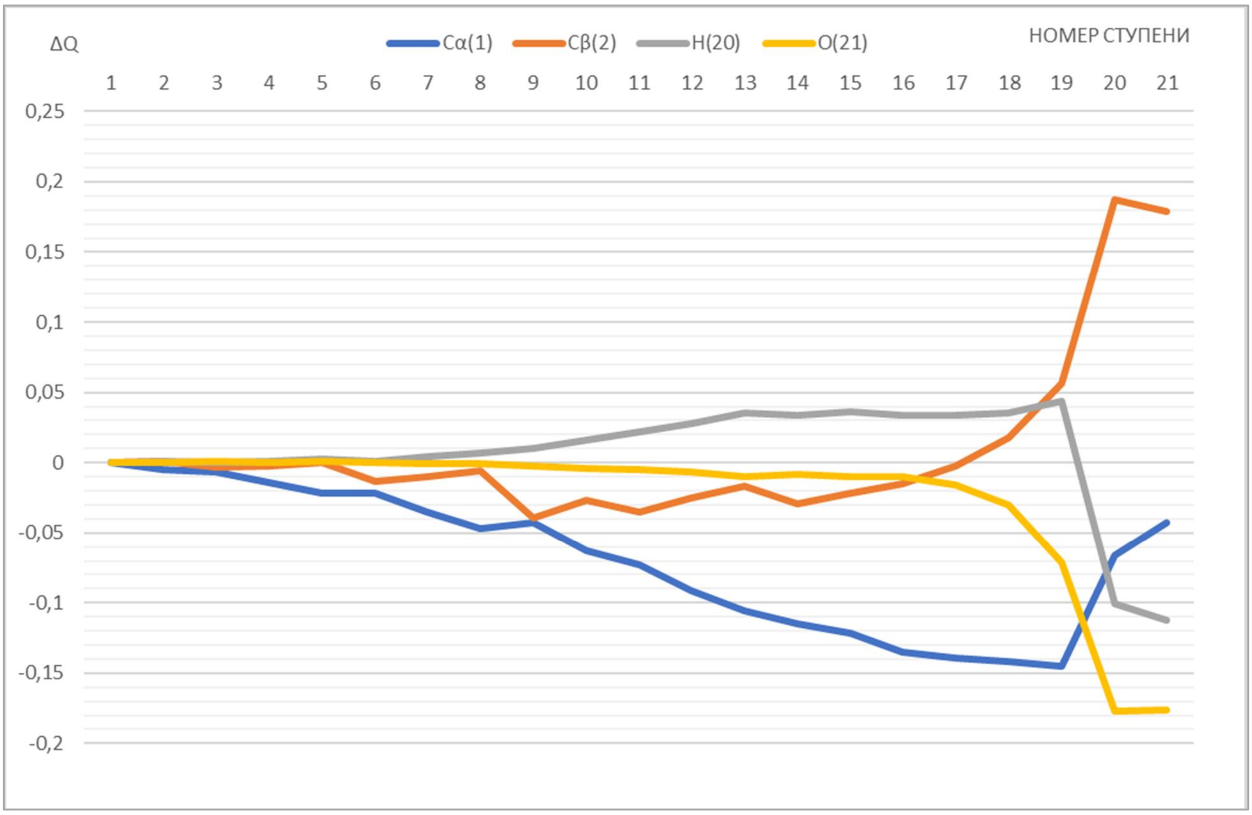

Figure 8. *Change in charges along reaction coordinate in system (II) having stoichiometric composition 1:1:1:1.*

Based on analysis of catalyst and monomer fragments behavior - breaking of a H-F bonds, formation of new ones (H-C_{α}), changes in total energy of molecular system along reaction coordinate (see Fig. 3) and charge redistribution (see Fig. 4) - it can be seen that in the former case (for BF_3-HF system, i.e. for *p*-methylstyrene–toluene) the initiation mechanism is the usual acceptance of a proton from the BF_3-HF complex, and its attachment to the most hydrogenated atom of *p*-methylstyrene, with simultaneous transformation of π-double bond of monomer to a single σ-bond (similarly to [10]).

In this case, as follows from Table 1, the amount of toluene practically does not affect the activation energy (it varies within the range of methodic error in the range of 73-79 kJ/mol), and also does not affect the initiation mechanism of cationic polymerization of *p*-methylstyrene in the presence of complex catalyst BF_3-HF.

Table 1. *Activation energy (Ea) and thermal effects (Q) of reaction in system (I).*

№	Stoichiometric composition of molecular system BF_3-HF - *p*-methylstyrene	Ea, kJ/mol	Q, kJ/mol
1	1:1:1:0	79	8
2	1:1:1:1	76	0
3	1:1:1:2	73	0

4	1:1:1:3	73	-6
5	1:1:1:4	78	-3

It should be noted the following trend: an increase in the amount of solvent – i.e. toluene, can change the nature of reaction - from endothermic to exothermic.

Table 2. *Activation energy (Ea) and thermal effects (Q) of reaction in system (II).*

№	Stoichiometric composition of molecular system BF_3- H_2O - *p*-methylstyrene	Ea, kJ/mol	Q, kJ/mol
1	1:1:1:0	134	115
2	1:1:1:1	136	116
3	1:1:1:2	123	86
4	1:1:1:3	116	76
5	1:1:1:4	118	86

Based on analysis of complex catalyst BF_3-H_2O and monomer fragments behavior - breaking of a O-H bond, transformation of π-bond of monomer into a σ-bond, and also formation of new O-C and C-H bonds, changes in total energy of molecular system along reaction coordinate (see Fig. 4), change in charges during reaction (see Fig. 6) - it can be seen that in this case the initiation mechanism is the coordinated process, accompanying by simultaneous breaking and formation of above bonds (similarly to [12]). In this case, the amount of toluene practically does not affect the initiation mechanism, but it very significantly affects the energy of this reaction. Regardless of the amount of toluene, the reactions are endothermic and have a barrier character. In this regard, the following dependence has been established: an increase in the amount of toluene in reaction system by 4 times reduces the activation energy from 134 kJ/mol to 116 kJ/mol, and the thermal effect of reaction - from 116 kJ/mol to 76 kJ/mol, respectively.

Obviously, the obtained results of quantum-chemical calculations at the nanoscale level for both systems (I and II) should be experimentally verified.

Conclusion

Thus, we first performed systematic studies of cationic polymerization initiation mechanism of *p*-methylstyrene in the presence of complex catalysts (BF_3-HF (I) and BF_3-H_2O (II) in toluene) in systems having different stoichiometric composition. It was found that for system (I), the amount of toluene does not affect the activation energy of this reaction, and the thermal effect increases with an increase in the amount of toluene; in such a case, this reaction can even turn from exothermic to exothermic.

In system (II), an increase in the amount of toluene leads to a decrease in activation energy and thermal effect.

Ultimately, the obtained dependences (together with the well-known method of controlling the olefin initiation reaction by varying the nature of ligand environment of Lewis acid (BF_3) and Bronsted (HF, H_2O) [13]) give new possibilities for controlling of reaction under study by changing the ratio between the catalyst and solvent (toluene) and also to obtain the polymer (*p*-methylstyrene) with predetermined properties.

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