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**MECHANISM FOR INITIATION CATION POLYMERIZATION OF
p-METYLSTYRENE IN THE PRESENCE OF $\text{BF}_3 \cdot \text{HF}$ CATALYST
IN TOLUENE AT 1: 1: 3 RATIO**

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Abstract: In this paper, initiation mechanism of cationic polymerization of *p*-methylstyrene in the presence of a complex catalyst $\text{BF}_3 \cdot \text{HF}$ in toluene at the ratio of 1: 1: 3 has been studied by *ab initio* method. The values of activation energies and reaction enthalpy are estimated.

Keywords: initiation mechanism, *p*-methylstyrene, boron fluoride catalyst - hydrogen fluoride, toluene, activation energy, enthalpy, *ab initio* method.

Introduction

Boron fluoride - hydrogen fluoride ($\text{BF}_3 \cdot \text{HF}$) is a typical catalyst for cationic polymerization [1], the classical stages of which are initiation, growth and termination of material chain [2]. It is obvious that varying the character of Lewis acid (for example, BF_3 , BF_2CH_3 , $\text{BF}(\text{CH}_3)_2$, $\text{B}(\text{CH}_3)_3$, BF_2CH_5 , etc.) and Brønsted acid (HF , HCl , HBr , etc.) in catalyst composition, as well as the stoichiometric composition "catalyst : solvent" (1: 1 (in this case - toluene), 1: 2, 1: 3, 1: 4, etc.) opens up in practice the possibility of controlling the polymerization process at initiation stage, up to obtaining a polymer (oligomer, telomer, and, in particular - poly-*p*-methylstyrene) with specified physicochemical properties. A number of important fundamental issues concerning the mechanisms

of elementary acts of cationic polymerization of *p*-methylstyrene: initiation, growth and termination of a chain in the presence of $\text{BF}_3 \cdot \text{HF}$ catalyst in toluene, remain unclear until now. And, in particular, the elucidation of energy dependence of initiation reaction for cationic polymerization of *p*-methylstyrene (E_A is activation energy, E_T is heat effect of reaction) on stoichiometric composition of molecular system “catalyst – solvent” ($\text{BF}_3 \cdot \text{HF}$ - toluene 1: 1, 1: 2, 1: 3, 1: 4, etc.).

The calculation of initiation mechanism of of stoichiometric compositions 1: 1 and 1: 2 (catalyst: solvent) was carried out in [3, 4]; therefore, the purpose of this paper is to study of initiation mechanism in the presence of this catalyst by calculating the reaction of interaction of monomer with initiator along $\text{R}_{\text{C1-H20}}$ coordinate in toluene with stoichiometric composition 1: 3 (within the framework of molecular model).

Methodical part

A quantum chemical study of initiation mechanism of *p*-methylstyrene was carried out by *ab initio* RHF/6-311G** method [5] in accordance with procedure, for example, described in [6 - 9], using software [10 - 12]. The reaction coordinate is $\text{R}_{\text{C(1)H(20)}}$.

Calculation results

The results of quantum chemical calculations (the initial model, the formed active center (AC), the energy profile of reaction, and the change in charges on the atoms directly involved in this reaction) are shown in Fig. 1-4 and in Table 1.

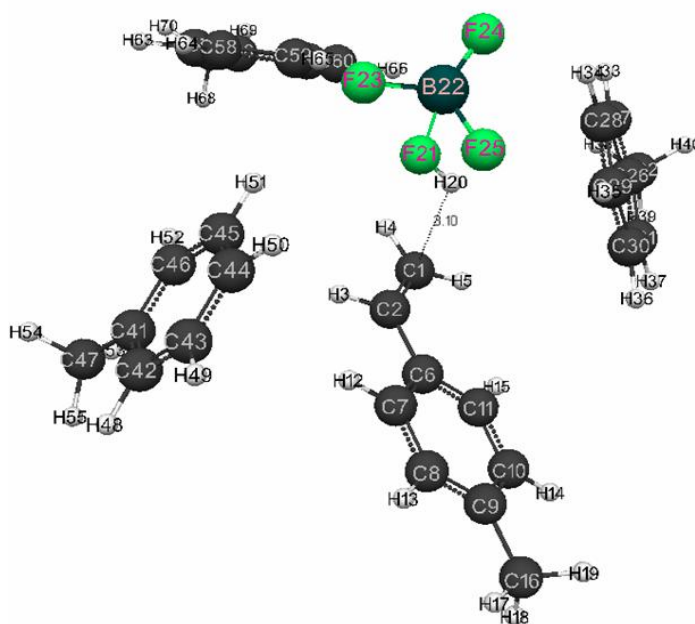


Figure 1. Model before interaction of complex catalyst $HF \cdot BF_3$ with *p*-methylstyrene in toluene with stoichiometric composition 1: 1: 3.

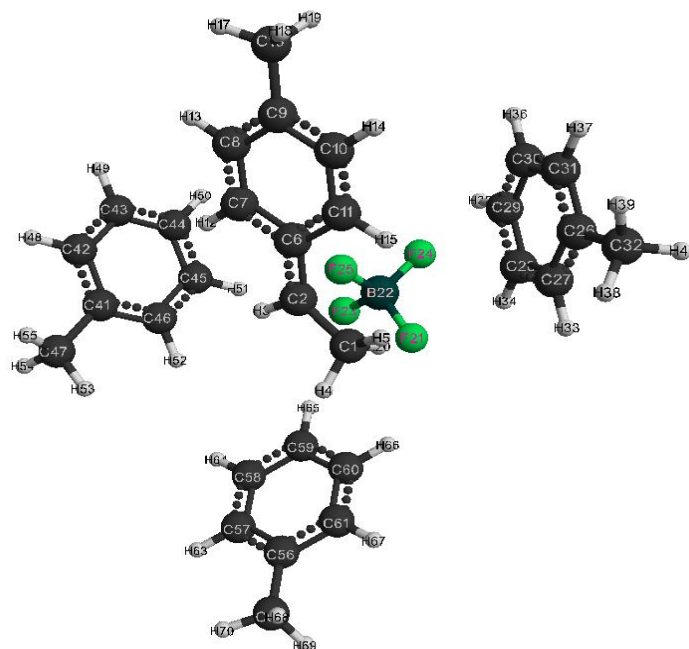


Figure 2. Model after reaction of $HF \cdot BF_3$ complex catalyst with *p*-methylstyrene in toluene with stoichiometric composition 1: 1: 3.

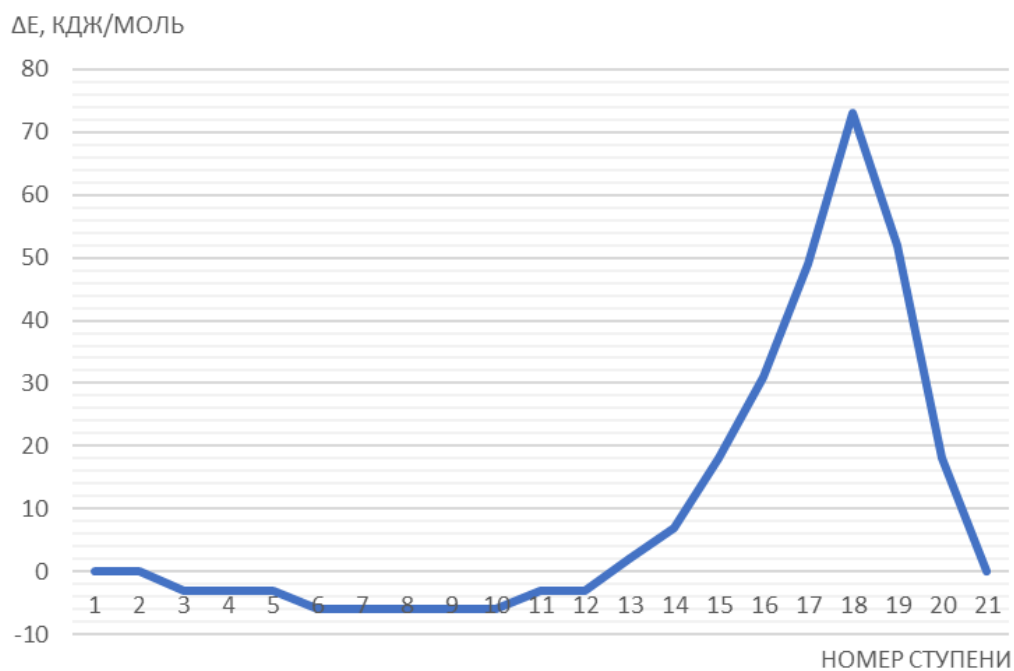


Figure 3. Change in total energy (DE) along the coordinate of reaction studied (No. 1-21 is interaction steps)

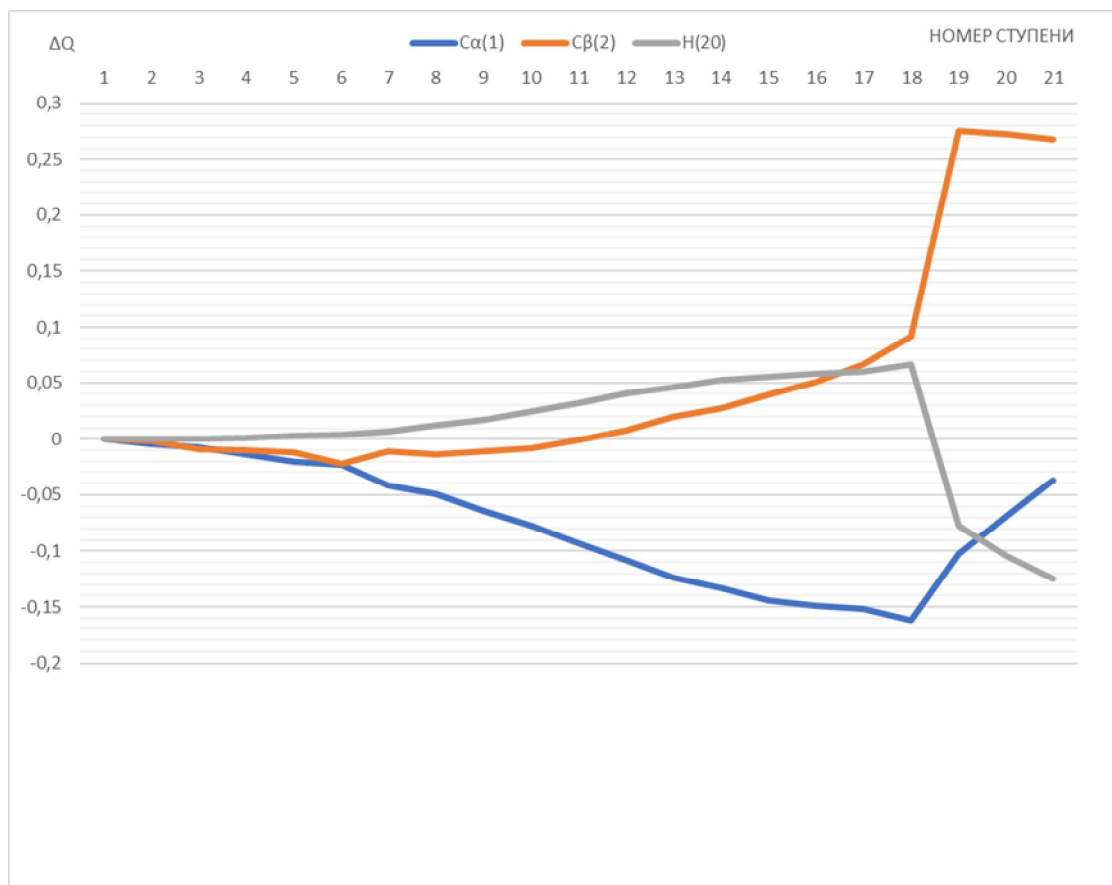


Figure 4. Changes in charges on atoms directly involved in reaction: C (1), C (2), H (20)

Table 1 shows the values of all charges on the atoms of molecular system at extremum points along the reaction coordinate $R_{H(20)-C(1)}$. From Table 1 it can be seen that the law of charge conservation clearly runs at each stage of components interaction.

Table 1. Atoms charges at extremum points (steps 1, 9, 18, 21).

Atom	No. of step			
	1	9	18	21
C(1)	-0,217	-0,281	-0,379	-0,254
C(2)	-0,148	-0,159	-0,056	0,120
H(3)	0,125	0,130	0,142	0,201
H(4)	0,128	0,143	0,157	0,135
H(5)	0,105	0,131	0,157	0,113
C(6)	-0,080	-0,089	-0,127	-0,204
C(7)	-0,066	-0,051	-0,025	0,063
C(8)	-0,096	-0,098	-0,102	-0,139
C(9)	-0,120	-0,115	-0,103	-0,046

C(10)	-0,095	-0,096	-0,100	-0,120
C(11)	-0,057	-0,044	-0,027	0,049
H(12)	0,133	0,138	0,139	0,191
H(13)	0,084	0,085	0,090	0,110
H(14)	0,083	0,085	0,092	0,111
H(15)	0,088	0,099	0,112	0,153
C(16)	-0,176	-0,177	-0,179	-0,187
H(17)	0,094	0,095	0,098	0,114
H(18)	0,106	0,108	0,111	0,122
H(19)	0,106	0,107	0,115	0,140
H(20)	0,358	0,375	0,424	0,233
F(21)	-0,339	-0,362	-0,479	-0,434
B(22)	0,827	0,826	0,873	0,847
F(23)	-0,272	-0,278	-0,305	-0,402
F(24)	-0,276	-0,273	-0,298	-0,391
F(25)	-0,276	-0,277	-0,307	-0,472
C(26)	-0,120	-0,120	-0,121	-0,124
C(27)	-0,094	-0,100	-0,099	-0,124
C(28)	-0,104	-0,092	-0,098	-0,114
C(29)	-0,180	-0,130	-0,136	-0,126
C(30)	-0,060	-0,088	-0,091	-0,086
C(31)	-0,100	-0,100	-0,095	-0,114
C(32)	-0,177	-0,177	-0,177	-0,172
H(33)	0,090	0,086	0,086	0,085
H(34)	0,117	0,113	0,123	0,144
H(35)	0,118	0,110	0,116	0,144
H(36)	0,106	0,097	0,093	0,091
H(37)	0,087	0,085	0,084	0,080
H(38)	0,103	0,098	0,098	0,093
H(39)	0,094	0,096	0,094	0,090
H(40)	0,113	0,112	0,112	0,115
C(41)	-0,114	-0,111	-0,112	-0,116
C(42)	-0,099	-0,108	-0,106	-0,118
C(43)	-0,083	-0,083	-0,086	-0,091
C(44)	-0,127	-0,120	-0,122	-0,137
C(45)	-0,093	-0,097	-0,106	-0,084
C(46)	-0,119	-0,123	-0,126	-0,170
C(47)	-0,176	-0,175	-0,175	-0,173
H(48)	0,084	0,086	0,086	0,084

H(49)	0,093	0,095	0,096	0,094
H(50)	0,100	0,103	0,110	0,106
H(51)	0,122	0,120	0,132	0,166
H(52)	0,094	0,095	0,094	0,116
H(53)	0,102	0,098	0,097	0,097
H(54)	0,110	0,112	0,113	0,116
H(55)	0,095	0,098	0,097	0,094
C(56)	-0,123	-0,122	-0,123	-0,126
C(57)	-0,091	-0,092	-0,092	-0,093
C(58)	-0,094	-0,091	-0,091	-0,101
C(59)	-0,108	-0,115	-0,119	-0,136
C(60)	-0,100	-0,100	-0,105	-0,112
C(61)	-0,095	-0,099	-0,099	-0,106
C(62)	-0,178	-0,178	-0,177	-0,176
H(63)	0,086	0,086	0,085	0,081
H(64)	0,098	0,098	0,098	0,095
H(65)	0,118	0,114	0,122	0,152
H(66)	0,096	0,105	0,110	0,131
H(67)	0,084	0,086	0,085	0,080
H(68)	0,110	0,109	0,107	0,096
H(69)	0,098	0,102	0,103	0,109
H(70)	0,097	0,096	0,094	0,090

Thus, in this paper we performed the quantum chemical study of initiation mechanism of cationic polymerization of *p*-methylstyrene under the action of complex catalyst $\text{BF}_3 \cdot \text{HF}$ with toluene in the 1: 1: 3 ratio by *ab initio* method. Analysis of change in charges on atoms directly involved in this reaction (see Fig. 4), behavior of reaction fragments, breaking and formation of new bonds indicate that mechanism under study is usual acceptance of $\text{H} (1)^+$ proton from $\text{BF}_3 \cdot \text{HF}$ catalyst and its addition to α -carbon monomer atom. The calculated values $E_A = 73 \text{ kJ/mol}$, $E_T = -6 \text{ kJ/mol}$.

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