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MECHANISM FOR INITIATION CATION POLYMERIZATION OF *p*-METHYLSTYRENE IN THE PRESENCE OF BF₃ · HF CATALYST IN TOLUENE AT 1:4 RATIO

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Abstract: In this paper, initiation mechanism of cationic polymerization of *p*-methylstyrene in the presence of a complex catalyst BF₃ · HF at the ratio of 1:4 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 (BF₃·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 variation in nature of Lewis acid (for example, BF₃, BF₂CH₃, BF(CH₃)₂, B(CH₃)₃, BF₂CH₅, 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 the possibility of controlling the polymerization process at initiation stage in practice up to obtaining a polymer (oligomer, telomer, and, in particular, poly-*p*-methylstyrene) with specified physico-chemical properties.

Until now, a number of important fundamental issues concerning the mechanisms of elementary acts of cationic polymerization of *p*-methylstyrene: initiation, chain propagation and chain termination in the presence of $\text{BF}_3 \cdot \text{HF}$ catalyst in toluene. And, in particular, the elucidation of stoichiometric composition influence of molecular system “catalyst – solvent” ($\text{BF}_3 \cdot \text{HF}$ - toluene 1:1, 1:2, 1:3, 1:4, etc.) on the energy of initiation reaction of cationic polymerization for *p*-methylstyrene (E_A is activation energy, E_T is thermal effect of reaction). The calculation of initiation mechanism for stoichiometric composition 1:1, 1:2, 1:3 (catalyst:solvent) was carried out in [3-5], therefore, the purpose of this paper is to study of initiation mechanism in the presence of this catalyst by calculating the interaction reaction of monomer and initiator along the $\text{RC}_{1-\text{H}_{20}}$ coordinate in toluene with stoichiometric composition of 1:4 (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 [6] in accordance with procedure, for example, described in [7–10] using software [11–13]. The reaction coordinate is $\text{RC}_{(1)\text{H}(20)}$.

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 Figs. 1-4 and in Table 1.

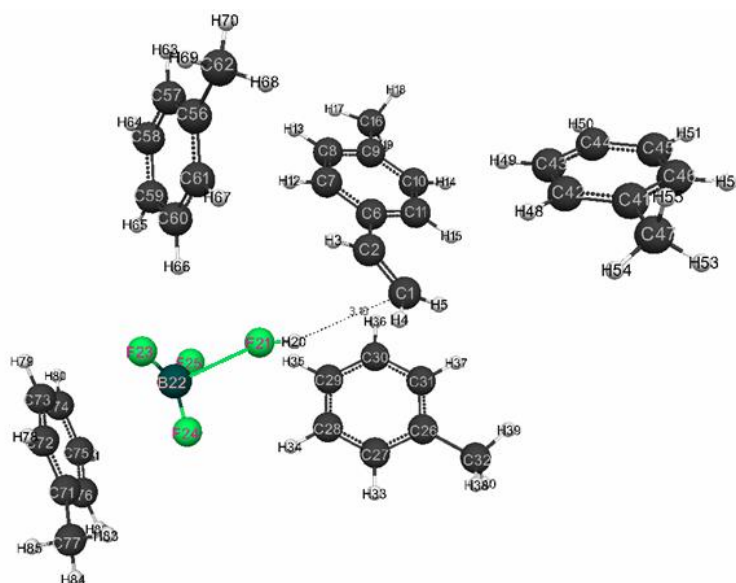


Figure 1. Initial model of interaction reaction of complex catalyst $\text{HF} \cdot \text{BF}_3$ with *p*-methylstyrene in toluene with stoichiometric composition of 1:4.

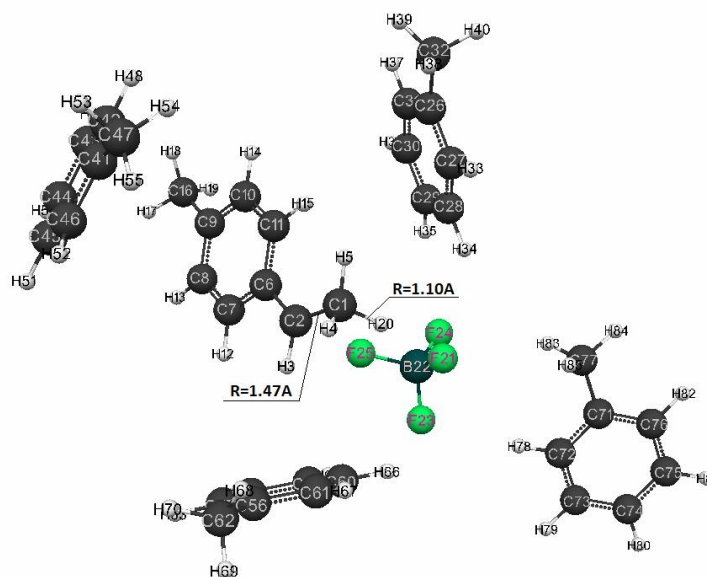


Figure 2. The result of reaction of complex catalyst $HF \cdot BF_3$ with *p*-methylstyrene in toluene with stoichiometric composition of 1:4.

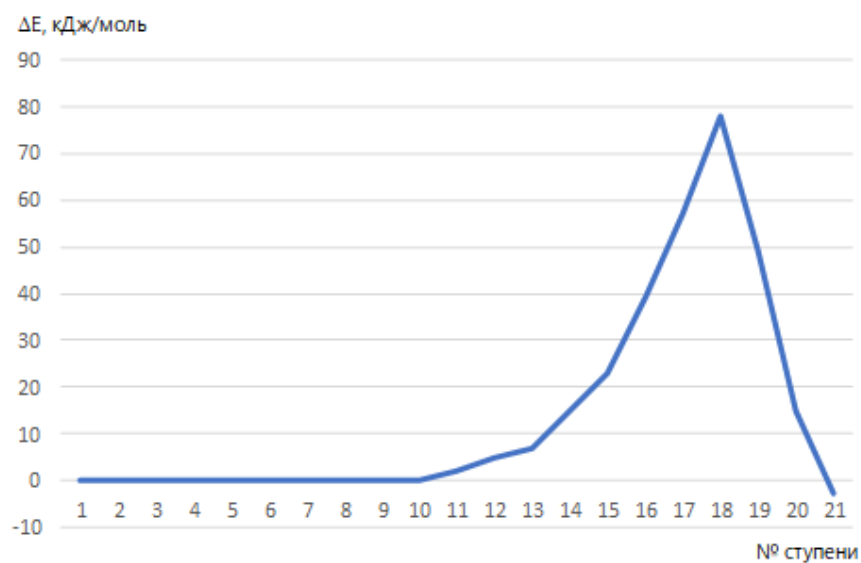


Figure 3. Change in total energy (DE) along the coordinate of reaction studied (No. 1-21 is interaction steps)

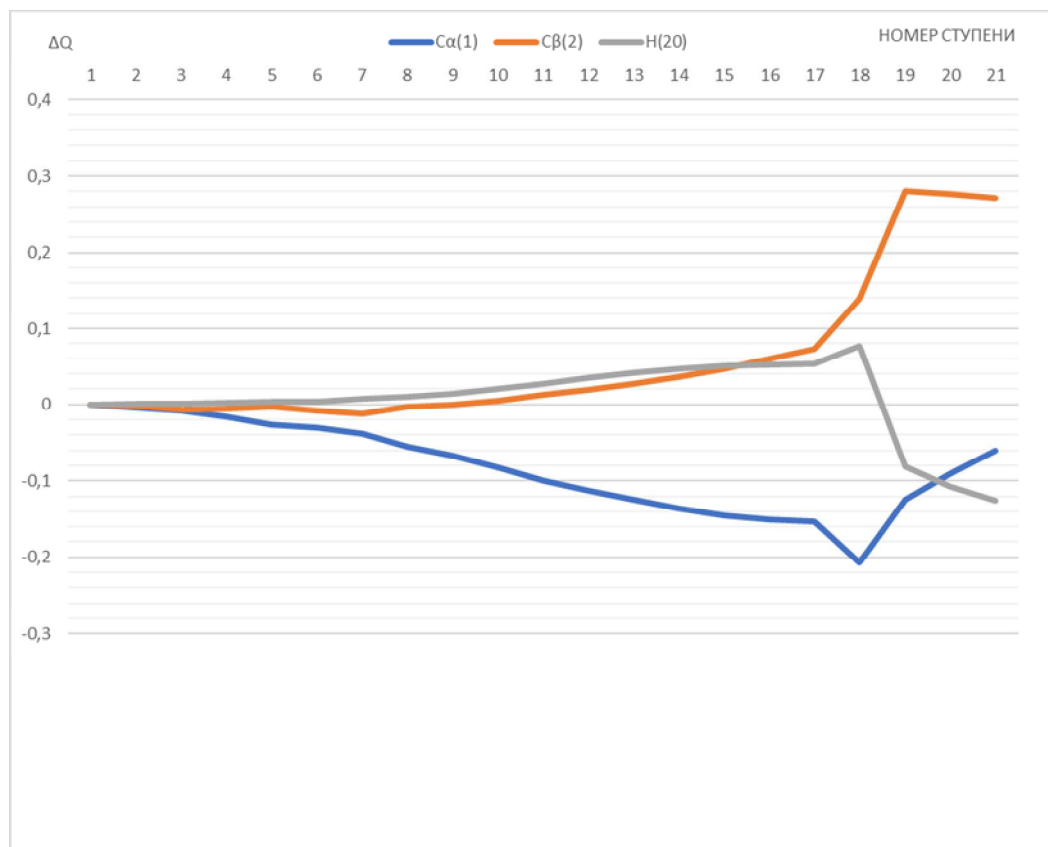


Figure 4. Changes in charges on atoms directly involved in reaction:
C(1), C(2), H(20)

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. Charges on the atoms at extremum points (steps 1, 8, 12, 18, 21).

Atom	No. of step			
	1	8	18	21
C(1)	-0,198	-0,253	-0,405	-0,258
C(2)	-0,153	-0,156	-0,014	0,118
H(3)	0,116	0,124	0,159	0,228
H(4)	0,114	0,128	0,152	0,129
H(5)	0,111	0,131	0,163	0,117
C(6)	-0,081	-0,086	-0,134	-0,178
C(7)	-0,063	-0,054	-0,015	0,056
C(8)	-0,100	-0,100	-0,105	-0,120
C(9)	-0,118	-0,117	-0,095	-0,048
C(10)	-0,097	-0,095	-0,104	-0,114
C(11)	-0,066	-0,056	-0,021	0,055
H(12)	0,143	0,143	0,132	0,135

H(13)	0,085	0,085	0,093	0,109
H(14)	0,084	0,086	0,097	0,110
H(15)	0,094	0,098	0,127	0,154
C(16)	-0,176	-0,177	-0,180	-0,188
H(17)	0,096	0,095	0,100	0,114
H(18)	0,110	0,108	0,111	0,118
H(19)	0,102	0,107	0,122	0,143
H(20)	0,353	0,363	0,429	0,227
F(21)	-0,340	-0,355	-0,438	-0,446
B(22)	0,843	0,842	0,869	0,886
F(23)	-0,278	-0,280	-0,333	-0,406
F(24)	-0,279	-0,276	-0,331	-0,403
F(25)	-0,276	-0,276	-0,346	-0,471
C(26)	-0,118	-0,119	-0,120	-0,121
C(27)	-0,091	-0,099	-0,103	-0,127
C(28)	-0,110	-0,095	-0,108	-0,112
C(29)	-0,176	-0,145	-0,123	-0,129
C(30)	-0,060	-0,074	-0,095	-0,085
C(31)	-0,104	-0,109	-0,096	-0,114
C(32)	-0,177	-0,176	-0,176	-0,173
H(33)	0,089	0,086	0,086	0,085
H(34)	0,118	0,114	0,126	0,151
H(35)	0,120	0,114	0,118	0,139
H(36)	0,105	0,098	0,094	0,091
H(37)	0,087	0,085	0,084	0,080
H(38)	0,099	0,097	0,098	0,092
H(39)	0,097	0,098	0,095	0,090
H(40)	0,113	0,112	0,112	0,115
C(41)	-0,123	-0,122	-0,124	-0,126
C(42)	-0,098	-0,100	-0,098	-0,096
C(43)	-0,090	-0,090	-0,089	-0,085
C(44)	-0,114	-0,114	-0,109	-0,107
C(45)	-0,084	-0,084	-0,083	-0,086
C(46)	-0,095	-0,094	-0,094	-0,093
C(47)	-0,178	-0,178	-0,178	-0,177
H(48)	0,087	0,087	0,086	0,088
H(49)	0,116	0,117	0,107	0,092
H(50)	0,093	0,092	0,092	0,091
H(51)	0,093	0,093	0,095	0,097
H(52)	0,085	0,085	0,086	0,090
H(53)	0,098	0,097	0,101	0,116
H(54)	0,096	0,096	0,095	0,099
H(55)	0,111	0,111	0,111	0,098
C(56)	-0,114	-0,113	-0,110	-0,119
C(57)	-0,100	-0,108	-0,111	-0,108
C(58)	-0,082	-0,082	-0,090	-0,102

C(59)	-0,127	-0,123	-0,118	-0,128
C(60)	-0,087	-0,090	-0,105	-0,112
C(61)	-0,113	-0,115	-0,120	-0,122
C(62)	-0,175	-0,174	-0,174	-0,171
H(63)	0,084	0,085	0,086	0,084
H(64)	0,093	0,095	0,098	0,096
H(65)	0,104	0,108	0,123	0,135
H(66)	0,117	0,116	0,122	0,140
H(67)	0,086	0,086	0,088	0,091
H(68)	0,101	0,100	0,097	0,094
H(69)	0,110	0,112	0,115	0,116
H(70)	0,095	0,096	0,096	0,092
C(71)	-0,109	-0,112	-0,134	-0,154
C(72)	-0,136	-0,124	-0,097	-0,096
C(73)	-0,093	-0,091	-0,098	-0,100
C(74)	-0,101	-0,105	-0,105	-0,107
C(75)	-0,080	-0,081	-0,089	-0,091
C(76)	-0,093	-0,093	-0,091	-0,090
C(77)	-0,177	-0,177	-0,196	-0,184
H(78)	0,093	0,091	0,123	0,143
H(79)	0,100	0,099	0,090	0,088
H(80)	0,095	0,094	0,088	0,083
H(81)	0,096	0,095	0,089	0,083
H(82)	0,087	0,087	0,081	0,076
H(83)	0,118	0,119	0,123	0,131
H(84)	0,094	0,094	0,093	0,074
H(85)	0,101	0,099	0,103	0,111

Thus, in this paper we performed the quantum chemical study of initiation mechanism of cationic polymerization of *n*-methylstyrene under the action of complex catalyst $\text{BF}_3 \cdot \text{HF}$ in the 1: 4 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 H^+ proton from $\text{BF}_3 \cdot \text{HF}$ catalyst and its addition to α -carbon monomer atom. The calculated values $E_A = 78 \text{ kJ/mol}$, $E_T = -3 \text{ kJ/mol}$.

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