ARTICLE INFO
Received 26 May 2021
Accepted 02 June 2021
Available online June 2021

MECHANISM FOR INITIATION CATION POLYMERIZATION OF *p*-METYLSTYRENE IN THE PRESENCE OF $BF_3 \cdot HF$ CATALYST IN TOLUENE AT 1: 1: 2 RATIO

[1]V.A. Babkin, [1]D.S. Andreev, [1]A.V. Ignatov, [1]S.Zh. Khachatryan, [2,3]E.S. Titova, [3]A.R. Titova, [2]A.I. Rakhimov, [2]V.T. Fomichev

[1]Volgograd State Technical University (Sebryakovsky br.), 403343 Volgograd Region, Mikhailovka, Michurina st., 21.
e-mail: babkin_v.a@mail.ru

[2]Volgograd State Technical University, 400005 Volgograd, Lenin av., 28.
e-mail: titova051@rambler.ru

[3]Volgograd State Medical University, 400131 Pavshikh Bortsov sq., 1.
e-mail: titova051@rambler.ru

Abstract: In this paper, initiation mechanism of cationic polymerization of *p*-methylstyrene in the presence of a complex catalyst $BF_3 \cdot HF$ in toluene at the ratio of 1: 1: 2 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 ($BF_3 \cdot HF$) 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, $BF(CH_3)_2$, $B(CH_3)_3$, 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 production of a polymer (oligomer, telomer, and, in particular - poly-*p*-methylstyrene) with specified physicochemical properties. In this regard, the aim of this paper is to study the initiation

mechanism of cationic polymerization of *p*-methylstyrene in toluene under the action of $BF_3 \cdot HF$ catalyst in the ratio “$BF_3 \cdot HF$ - *p*-methylstyrene (1): toluene (2)”, and to calculate the activation energies (E_A) and the enthalpy (ΔH) of reaction, which cannot be determined experimentally. The initiation mechanism for $BF_3 \cdot HF$ - *p*-methylstyrene - toluene system with stoichiometric composition 1: 1: 1 was studied in [3].

Methodical part

A quantum chemical study of initiation mechanism of *p*-methylstyrene was carried out by *ab initio* RHF/6-311G** method [4] in accordance with procedure, for example, described in [5-8], using software [9-11]. The reaction coordinate is $R_{C(1)H(20)}$.

Calculation results

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

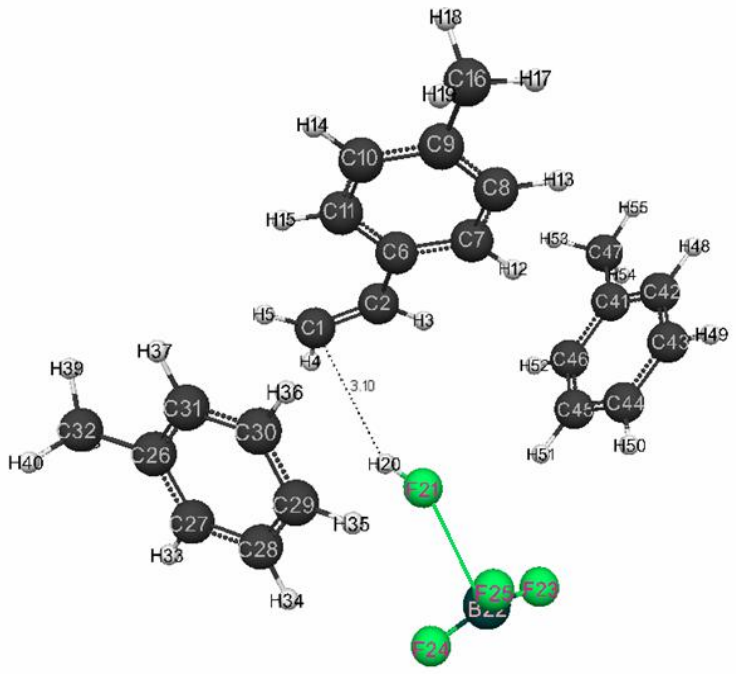

Figure 1. *Initial model of interaction reaction of complex catalyst $HF \cdot BF_3$ with p-methylstyrene in toluene with stoichiometric composition 1: 1: 2.*

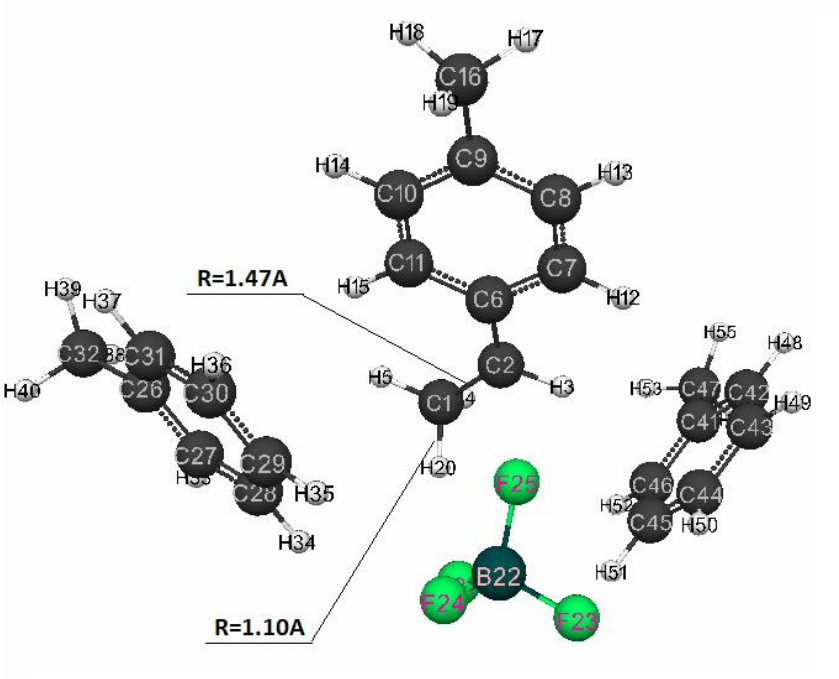

Figure 2. *The result of reaction of complex catalyst HF · BF_3 with p-methylstyrene in toluene with stoichiometric composition 1: 1: 2.*

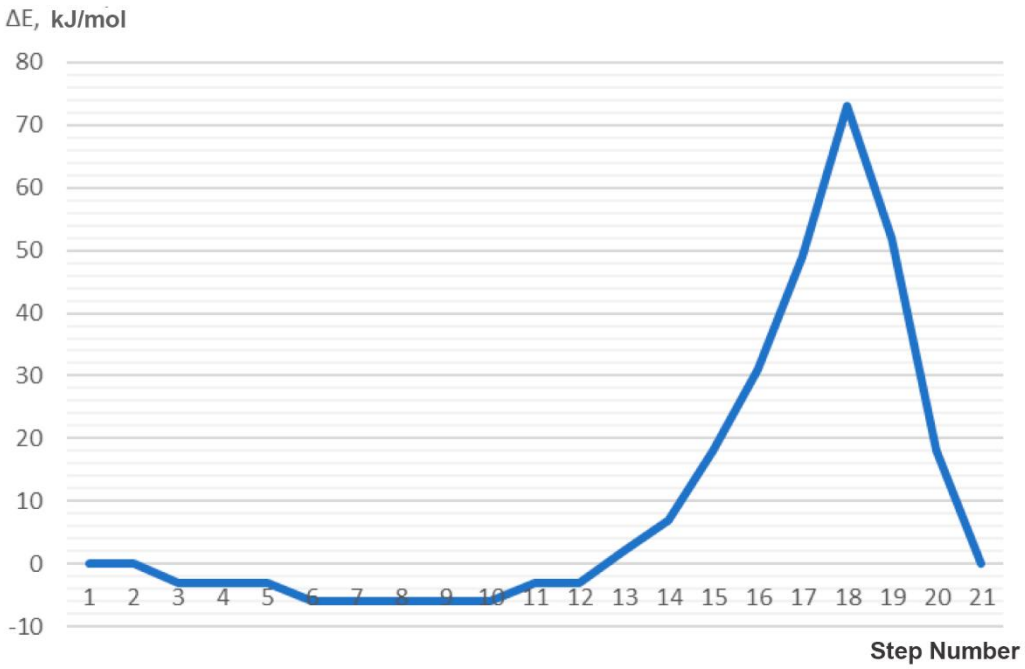

Figure 3. *Change in total energy (DE) along the coordinate of studied reaction (No. 1-21 - interaction steps).*

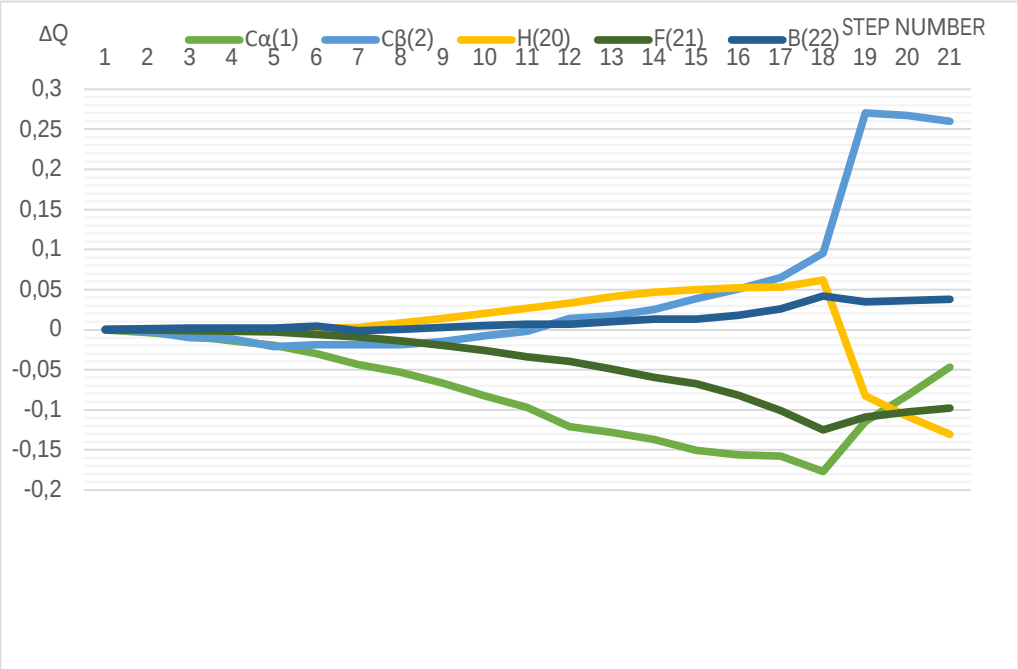

Figure 4. *Changes of atoms charges directly involved in reaction: C (1), C (2), H (20), F (21) and B (22).*

The values of all atoms charges of the molecular system at extremum points along the reaction coordinate $R_{H(20)-C(1)}$ are listed in Table 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, 12, 18, 21).*

Atom	**No. of step**				
	1	**9**	**12**	**18**	**21**
$C(1)_{\alpha}$	-0,210	-0,277	-0,331	-0,387	-0,257
$C(2)_{\beta}$	-0,136	-0,151	-0,122	-0,041	0,124
H(3)	0,122	0,127	0,128	0,144	0,232
H(4)	0,114	0,130	0,136	0,146	0,129
H(5)	0,107	0,136	0,150	0,163	0,118
C(6)	-0,090	-0,088	-0,095	-0,134	-0,181
C(7)	-0,063	-0,052	-0,045	-0,024	0,052
C(8)	-0,097	-0,098	-0,097	-0,100	-0,120
C(9)	-0,120	-0,116	-0,114	-0,102	-0,051
C(10)	-0,095	-0,096	-0,096	-0,102	-0,118
C(11)	-0,051	-0,043	-0,044	-0,017	0,048
H(12)	0,135	0,138	0,132	0,122	0,137
H(13)	0,084	0,085	0,086	0,090	0,110
H(14)	0,082	0,085	0,086	0,092	0,110

H(15)	0,088	0,097	0,104	0,122	0,153
C(16)	-0,176	-0,177	-0,178	-0,180	-0,187
H(17)	0,094	0,095	0,095	0,098	0,116
H(18)	0,108	0,107	0,109	0,111	0,118
H(19)	0,105	0,109	0,109	0,117	0,142
H(20)	0,357	0,371	0,390	0,419	0,227
F(21)	-0,343	-0,363	-0,383	-0,468	-0,441
B(22)	0,821	0,824	0,828	0,863	0,859
F(23)	-0,269	-0,273	-0,276	-0,302	-0,403
F(24)	-0,274	-0,272	-0,276	-0,301	-0,398
F(25)	-0,278	-0,277	-0,280	-0,316	-0,482
C(26)	-0,121	-0,120	-0,120	-0,121	-0,124
C(27)	-0,090	-0,099	-0,100	-0,100	-0,122
C(28)	-0,115	-0,098	-0,097	-0,109	-0,112
C(29)	-0,176	-0,136	-0,132	-0,129	-0,125
C(30)	-0,058	-0,084	-0,089	-0,091	-0,087
C(31)	-0,099	-0,105	-0,098	-0,092	-0,116
C(32)	-0,177	-0,176	-0,177	-0,177	-0,173
H(33)	0,090	0,087	0,087	0,087	0,086
H(34)	0,118	0,113	0,114	0,123	0,146
H(35)	0,119	0,116	0,114	0,117	0,141
H(36)	0,103	0,096	0,095	0,093	0,090
H(37)	0,088	0,085	0,085	0,084	0,080
H(38)	0,102	0,097	0,098	0,099	0,093
H(39)	0,094	0,096	0,096	0,094	0,090
H(40)	0,115	0,112	0,112	0,112	0,115
C(41)	-0,115	-0,113	-0,113	-0,114	-0,120
C(42)	-0,099	-0,107	-0,107	-0,105	-0,105
C(43)	-0,088	-0,084	-0,086	-0,088	-0,102
C(44)	-0,121	-0,120	-0,117	-0,119	-0,139
C(45)	-0,083	-0,091	-0,094	-0,104	-0,116
C(46)	-0,110	-0,115	-0,113	-0,116	-0,118
C(47)	-0,176	-0,174	-0,175	-0,175	-0,172
H(48)	0,084	0,086	0,086	0,086	0,084
H(49)	0,094	0,095	0,096	0,096	0,095
H(50)	0,105	0,108	0,111	0,121	0,142
H(51)	0,111	0,114	0,112	0,120	0,142
H(52)	0,086	0,087	0,087	0,087	0,090
H(53)	0,104	0,096	0,096	0,097	0,094

H(54)	0,109	0,113	0,113	0,114	0,116
H(55)	0,093	0,099	0,098	0,096	0,092

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 $BF_3 \cdot HF$ with toluene in the 1: 1: 2 ratio by *ab initio* method. Analysis of atoms charges changes directly involved in this reaction (see Figure 4), behavior of reaction fragments, breaking and formation of new bonds indicate that the mechanism under study is usual acceptance of H $(1)^+$ proton from $BF_3 \cdot HF$ catalyst and its addition to α-carbon monomer atom. The calculated values E_A = 73 kJ/mol, ΔH = 0 kJ/mol.

References

1. Kennedy, J., Cationic polymerization of olefins. Mir Publishing House, Moscow, **1978**, 431 p. (in Russian)

2. Odian, G., Principles of polymerization, Mir Publishing House, Moscow, **1974**, 614 p. (in Russian)

3. Babkin, V.A., Andreev D.S., Ignatov A.V. and others, Calculation of interaction mechanism for complex catalyst HF-BF_3 with *p*-methylstyrene in toluene with stoichiometric composition 1:1:1 by *ab initio* method, Fluorine Notes, **2021**, 2(135), 3-4.

4. Cirelson V.G., Quantum Chemistry. Molecules, molecular systems and solids, Moscow, Publishing House «Binom», **2010**, 496 p. (in Russian)

5. V. A. Babkin and others, Quantum-chemical research of the interaction mechanism of the complex catalyst chloride aluminium-hydrochloric acid and *p*-methylstyrene in toluene by the *ab initio* method, Oxidation Communications, **2020**, 43(2), 171-176.

6. V. A. Babkin and others, Quantum chemical calculation of initiation mechanism of cationic polymerisation of propylene with chloride-aluminium aquacomplex, Oxidation Communications, **2020,** 43(1), 24-29.

7. V. A. Babkin and others, Quantum chemical investigation of the initiation mechanism of the cationic polymerisation of 4-methylpentene-1 with chloride-aluminum aquacomplex, Oxidation Communications, **2019**, 42(3),275-281.

8. V. A. Babkin and others, On the mechanism of cationic polymerisation of *p*-isopropylstyrene in the presence of a complex catalyst boron fluoride-water, Oxidation Communications, **2019**, 42(1), 56-62.

9. Granovsky, A. A., Firefly version 8, **2013**. http://classic.chem.msu.su/gran/firefly/index.html

10. M.W. Schmidt and others, General Atomic and Molecular Electronic Structure System, J. Comput. Chem., **1993**, 14, 1347-1363.

11. B.M. Bode, M.S. Gordon, MacMolPlt: A Graphical User Interface for GAMESS, Journal of Molecular Graphics, **1998**, 16, 133-138.