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STUDY OF INTERACTION OF COMPLEX HF·BF_3 -CATALYST WITH *n*-METHYLSTYROL *AB INITIO* METHOD

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Abstract: A quantum chemical study of cationic polymerization monomer protonation of *p*-methylstyrene (in the presence of complex catalyst - boron fluoride/hydrogen fluoride (HF·BF_3) - with stoichiometric composition 1: 1) by *ab initio* method along the reaction coordinate $R_{C1\text{-}H20}$ was first performed. The protonation energy barrier (79 kJ/mol) and the thermal effect of this endothermic reaction (-8 kJ/mol) were calculated. The reaction is endothermic.

Keywords: *p*-methylstyrene, protonation, boron fluoride/hydrogen fluoride catalyst, reaction heat, *ab initio* method.

Introduction

The study of elementary events behavior of cationic *p*-methylstyrene polymerization in the presence of complex catalyst BF_3·HF is one of the most important fundamental problems in the

field polymerization for this monomer [**1**]. The aim of this work is to study the first stage - i.e. the initiation of p-methylstyrene in the presence of this complex catalyst by studying the interaction of monomer with initiator along the RC1-H20 coordinate in gas phase (within framework of molecular model).

Methodology

The mechanism of cationic polymerization monomer protonation of *p*-methylstyrene in the presence of complex $HF{\cdot}BF_3$ catalyst was studied. The distance between the C(1) and H(20) atoms was chosen as reaction coordinate. The calculation was performed using *ab initio* RHF/6-311G** quantum-chemical method [**2**], with geometry optimization for all parameters by gradient method integrated into Firefly program [**3**], based on GAMESS source code [**2, 4**]. This method was chosen because it allows you to accurately calculate the reaction energy barriers and active centers [**4**]. Calculations were performed in the approximation of an isolated molecule in the gas phase within the framework of the molecular model. The mechanism of protonation of *p*-methylstyrene was carried out according to the method described in detail in [**5**] and used in [**6-7**]. For visual molecular representation the MacMolPlt program was used [**8**].

Calculation data

The change in bond lengths along the protonation path, valence angles and atomic charges of molecular system during interaction of *p*-methylstyrene with catalyst $BF_3{\cdot}HF$ are presented in Table 1-3.

The reaction can be divided into three stages: the first stage is the coordination stage (see steps 1–7, Fig. 3), the second stage is the stage of π-bond breaking in monomer (steps 8–17), and the third stage is the stage of formation of active center (AC) (steps 18– 21).

The atoms C(1), C(2), H(20), O(21) and B(23) are directly involved in this interaction. Let us analyze the change in charges on these atoms along the interaction path of *p*-methylstyrene with the $BF_3{\cdot}HF$ catalyst.

At 1st stage (steps 1–7), the atomic charge on C(1) changes from –0.202 to –0.233; at 2nd of AC formation (stage 2, steps 8–17) - from –0.246 to –0.356; at 3rd stage of final product formation (stage 3, steps 18-21) - from -0.364 to -0.221.

At 1st stage the atomic charge on C(2) changes from -0.176 to -0.178; at 2nd stage - from -0.170 to -0.055; at 3rd stage - from -0.027 to 0.114.

At 1st stage (steps 1–7) the charge on H(20) changes from 0.343 to 0.356, at 2nd stage of AC formation (stage 2, stages 8–17), from 0.361 to 0.404; at 3rd stage of final product formation (stage 3, steps 18-21) - from 0.408 to 0.206.

At 1st stage the atomic charge on F(21) changes from -0.331 to -0.349; at 2nd stage - from -0.354 to -0.431; at 3rd stage - from -0.454 to -0.468.

At 1st stage (steps 1–7) the atomic charge on B(22) remains practically unchanged (from 0.809 to 0.810); at the stage of AC formation (stage 2, steps 8–17), from 0.810 to 0.823, at 2nd stage of final product formation (stage 3, steps 18-21) - from 0.835 to 0.848.

During of reaction, the F(21) -H(20) bonds are simultaneously broken, the C(1) -C(2) changes from double π-bond to a single σ-bond, the new bond C(1) - H(20) and the counterion [BF_3·F] is formed (Fig. 2).

The activation energy of reaction is 79 kJ/mol and thermal effect is -8 kJ/mol. The changes in atomic charges, behavior of reaction fragments, breaks and the formation of new bonds indicate that the reaction represents the usual proton acceptance from complex catalyst HF·BF_3 and protonation to the most hydrogenated carbon atom C(1).

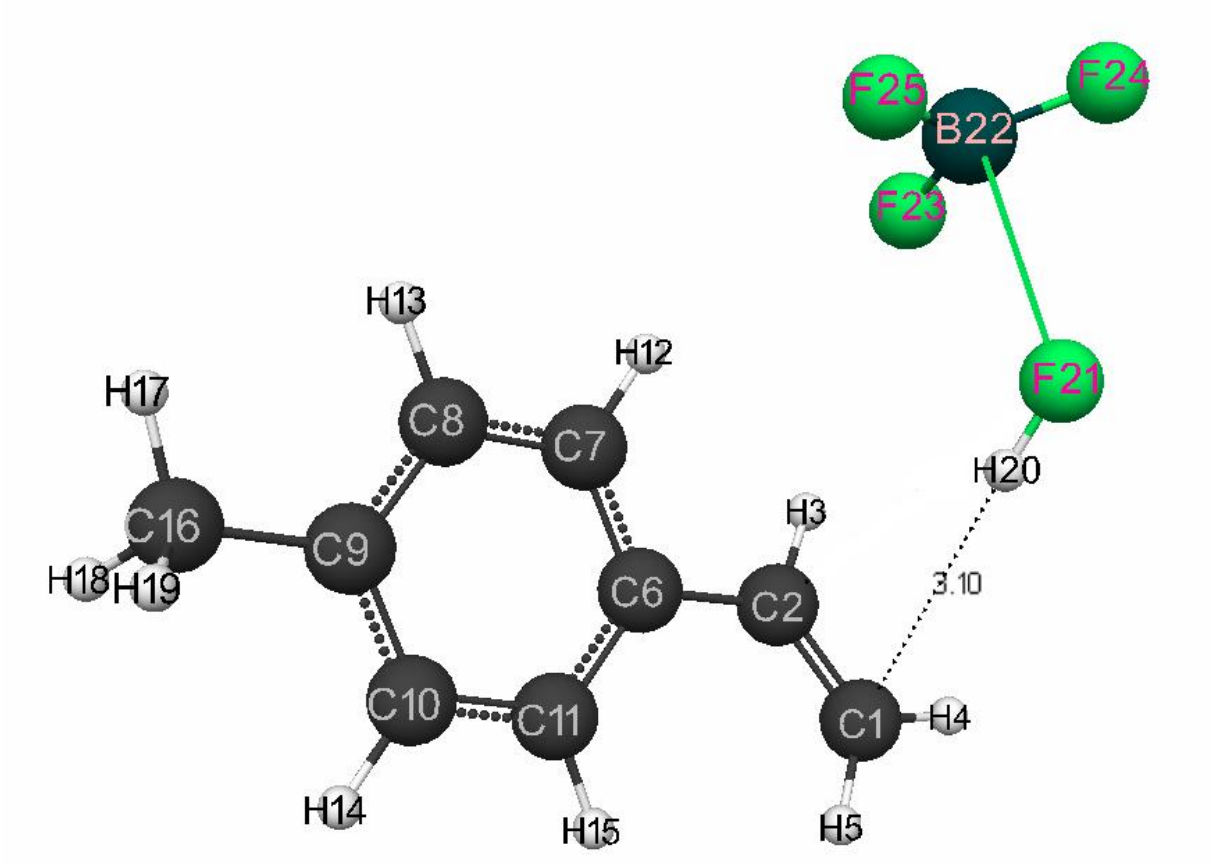

Figure 1. *The structure of initial model of complex catalyst HF · BF_3 with p-methylstyrene.*

In Fig. 1 are presents the geometric and electronic structure of initial model of *p*-methylstyrene, in Fig. 2 - the its structure after interaction of catalyst with *p*-methylstyrene, in Fig. 3 - the energy profile of the studied reaction, and in Fig. 4 – the changes in charges of atoms directly involved in the interaction of complex catalyst $HF{\cdot}BF_3$ with *p*-methylstyrene.

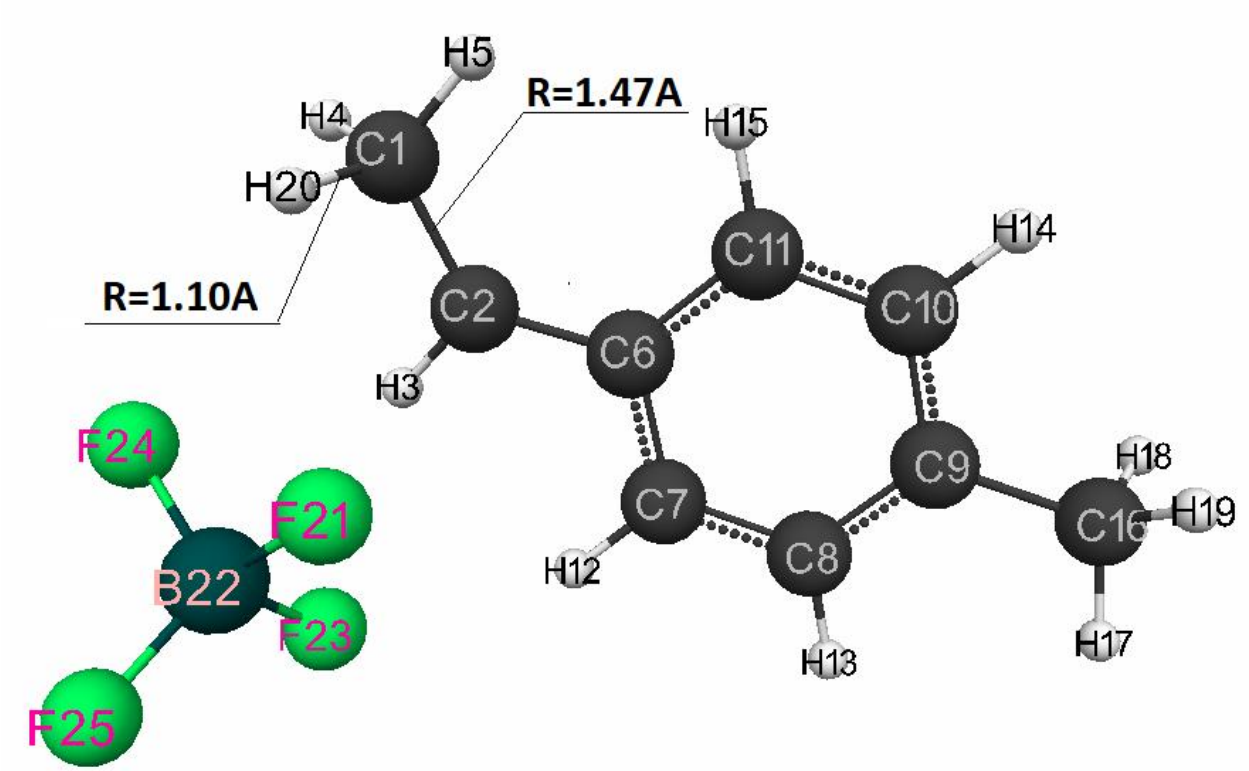

Figure 2. *The final interaction structure of complex catalyst $HF{\cdot}BF_3$ with p-methylstyrene.*

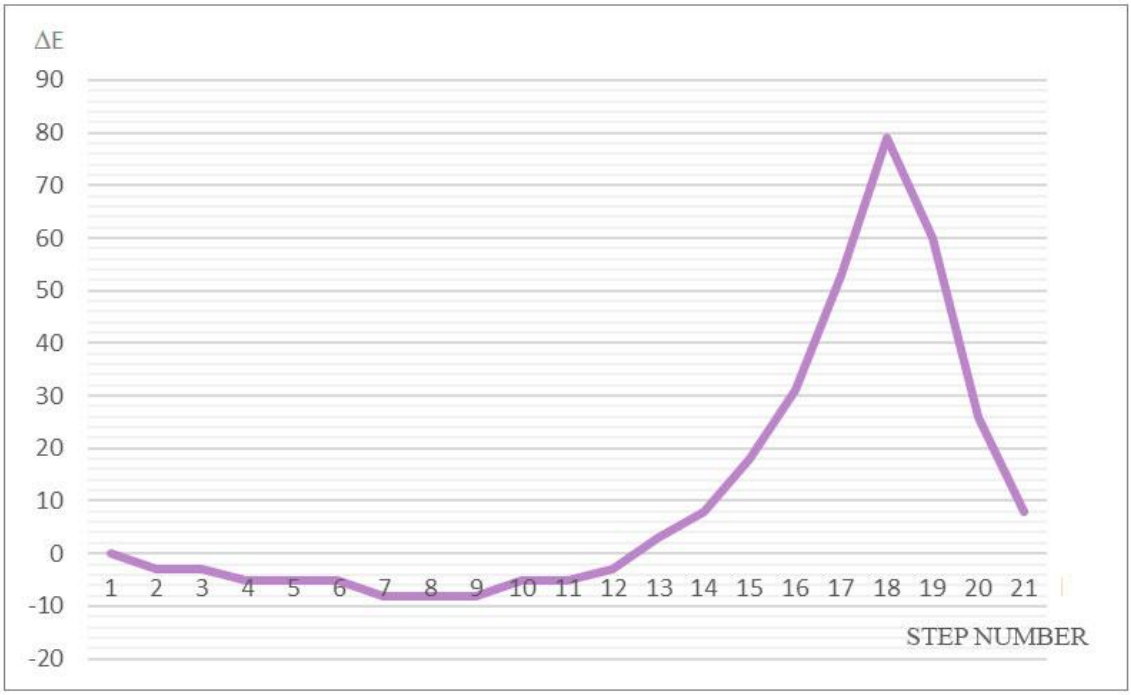

Figure 3. *The total energy change (DE) of studied reaction (1-21 is the steps of interaction).*

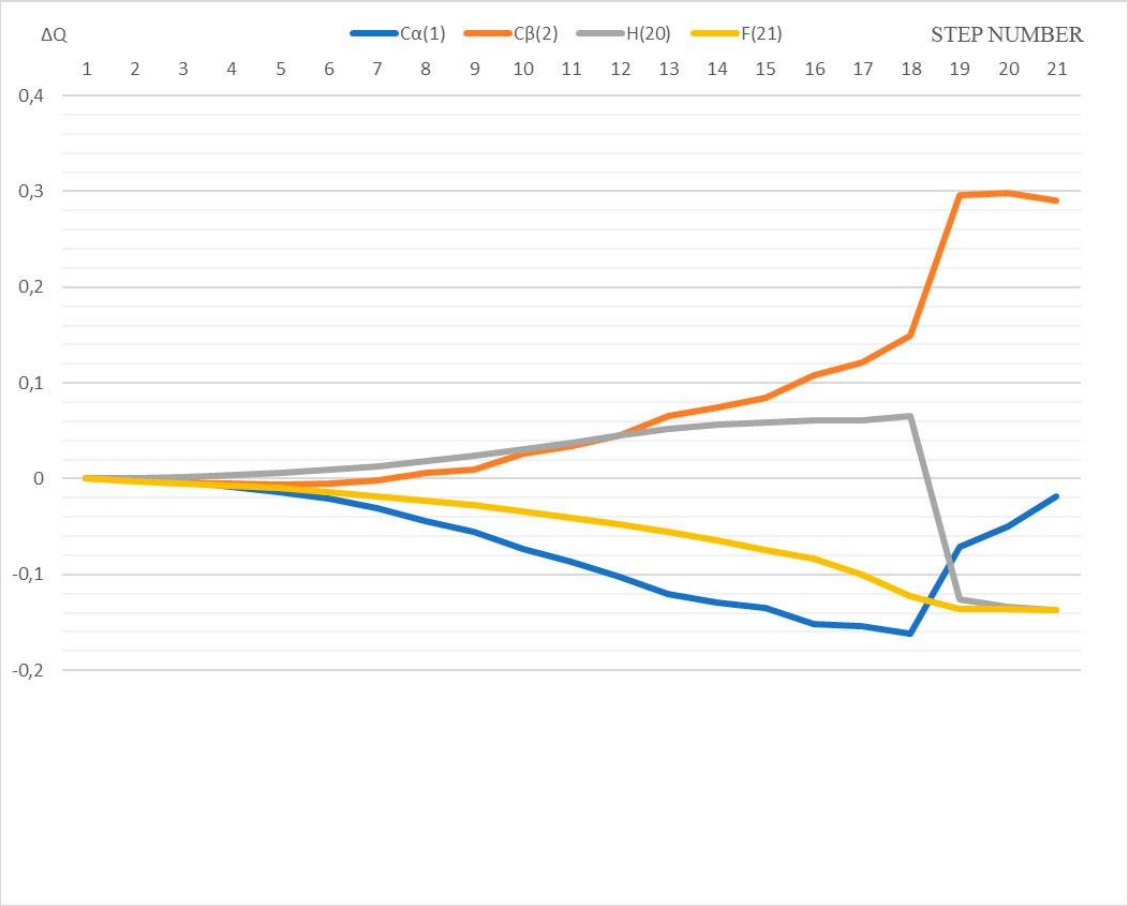

Figure 4. *The change in charges on some atoms along the reaction interaction path of complex catalyst $HF{\cdot}BF_3$ with p-methylstyrene.*

Table 1. *The change in bond lengths along the reaction interaction path of complex catalyst $HF{\cdot}BF_3$ with p-methylstyrene*

№ of step	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C(2)-C(1)	1,32	1,33	1,33	1,33	1,33	1,33	1,33	1,33	1,33	1,33
H(3)-C(2)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(4)-C(1)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(5)-C(1)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
C(6)-C(11)	1,40	1,40	1,40	1,40	1,40	1,40	1,39	1,39	1,39	1,39
C(6)-C(2)	1,48	1,48	1,48	1,48	1,48	1,48	1,48	1,48	1,48	1,48
C(7)-C(6)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
C(8)-C(7)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
C(9)-C(8)	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38
C(10)-C(9)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39
C(11)-C(10)	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38

H(12)-C(7)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(13)-C(8)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(14)-C(10)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(15)-C(11)	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07
C(16)-C(9)	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51
H(17)-C(16)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(18)-C(16)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(19)-C(16)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09
H(20)-F(21)	0,90	0,90	0,90	0,90	0,90	0,90	0,91	0,91	0,91	0,91
B(22)-F(21)	2,43	2,42	2,42	2,42	2,41	2,41	2,40	2,39	2,38	2,37
F(23)-B(22)	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,31
F(24)-B(22)	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,30
F(25)-B(22)	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,30
H(20)-C(1)	3,10	3,00	2,90	2,80	2,70	2,60	2,50	2,40	2,30	2,20

Continuation of ***Table 1.***

№ of step	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
C(2)-C(1)	1,33	1,33	1,33	1,33	1,33	1,33	1,33	1,33	1,46	1,47	1,47
H(3)-C(2)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,07	1,07	1,07
H(4)-C(1)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,09
H(5)-C(1)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
C(6)-C(11)	1,39	1,39	1,39	1,39	1,39	1,40	1,40	1,40	1,42	1,42	1,42
C(6)-C(2)	1,48	1,48	1,48	1,48	1,48	1,47	1,47	1,47	1,40	1,40	1,39
C(7)-C(6)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,41	1,41	1,41
C(8)-C(7)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,38	1,38	1,38	1,38
C(9)-C(8)	1,39	1,39	1,39	1,39	1,39	1,38	1,39	1,39	1,39	1,39	1,39
C(10)-C(9)	1,39	1,39	1,39	1,39	1,39	1,39	1,39	1,40	1,41	1,41	1,41
C(11)-C(10)	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,38	1,36	1,36	1,36
H(12)-C(7)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,07	1,07	1,07
H(13)-C(8)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,07	1,07	1,07
H(14)-C(10)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,07	1,07	1,07
H(15)-C(11)	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07
C(16)-C(9)	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,50	1,50	1,50

H(17)-C(16)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(18)-C(16)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,08	1,09
H(19)-C(16)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,08
H(20)-F(21)	0,91	0,92	0,92	0,93	0,93	0,94	0,96	1,00	2,45	2,54	2,52
B(22)-F(21)	2,35	2,34	2,32	2,30	2,27	2,24	2,18	1,99	1,41	1,41	1,41
F(23)-B(22)	1,31	1,31	1,31	1,31	1,31	1,31	1,31	1,32	1,41	1,41	1,41
F(24)-B(22)	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,31	1,40	1,40	1,40
F(25)-B(22)	1,30	1,30	1,30	1,30	1,30	1,30	1,30	1,31	1,35	1,35	1,35
H(20)-C(1)	2,10	2,00	1,90	1,80	1,70	1,60	1,50	1,40	1,30	1,20	1,10

Table 2. *The change in valence angles along the reaction interaction coordinate of complex catalyst HF·BF_3 with p-methylstyrene.*

№ of step	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
H(3)-C(2)-C(1)	118	118	118	118	118	118	118	118	118	118
H(4)-C(1)-C(2)	121	121	121	121	121	121	121	121	121	121
H(5)-C(1)-C(2)	123	123	123	123	123	123	123	123	123	123
C(6)-C(11)-C(10)	121	121	121	121	121	121	121	121	121	121
C(6)-C(2)-C(1)	127	127	127	127	127	127	127	127	127	127
C(7)-C(6)-C(11)	118	118	118	118	118	118	118	118	118	118
C(8)-C(7)-C(6)	121	121	121	121	121	121	121	121	121	121
C(9)-C(8)-C(7)	121	121	121	121	121	121	121	121	121	121
C(10)-C(9)-C(8)	118	118	118	118	118	118	118	118	118	118
C(11)-C(10)-C(9)	121	121	121	121	121	121	121	121	121	121
H(12)-C(7)-C(6)	120	120	120	120	120	120	120	120	120	120
H(13)-C(8)-C(7)	119	119	119	119	119	119	119	119	119	119
H(14)-C(10)-C(9)	119	119	119	119	119	119	120	120	119	119
H(15)-C(11)-C(10)	119	119	119	119	119	119	119	119	119	119
C(16)-C(9)-C(8)	122	122	122	122	122	122	122	121	121	121
H(17)-C(16)-C(9)	111	111	111	111	111	111	111	111	111	111
H(18)-C(16)-C(9)	111	111	111	111	111	111	111	111	111	111
H(19)-C(16)-C(9)	111	111	111	111	111	111	111	111	111	111
H(20)-C(1)-C(2)	66	67	67	68	69	71	72	74	75	77
F(23)-B(22)-F(21)	91	90	90	90	90	90	90	90	91	91

F(24)-B(22)-F(21)	93	93	93	93	93	93	93	93	93	93
F(25)-B(22)-F(21)	93	93	93	94	94	94	94	94	94	94

Continuation of ***Table 2.***

№ of step	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
H(3)-C(2)-C(1)	118	118	118	118	118	118	118	117	115	115	115
H(4)-C(1)-C(2)	121	121	121	121	121	120	120	120	113	111	109
H(5)-C(1)-C(2)	123	122	123	123	123	123	122	122	117	116	115
C(6)-C(11)-C(10)	121	121	121	121	121	121	121	121	120	120	120
C(6)-C(2)-C(1)	127	127	127	127	127	127	127	127	128	128	129
C(7)-C(6)-C(11)	118	118	118	118	118	118	118	118	119	119	119
C(8)-C(7)-C(6)	121	121	121	121	121	121	121	121	120	120	120
C(9)-C(8)-C(7)	121	121	121	121	121	121	121	121	120	120	120
C(10)-C(9)-C(8)	118	118	118	118	118	118	118	118	120	120	120
C(11)-C(10)-C(9)	121	121	121	121	121	121	121	121	121	120	120
H(12)-C(7)-C(6)	120	120	120	120	120	120	120	120	119	119	119
H(13)-C(8)-C(7)	119	119	119	119	119	119	119	119	120	120	120
H(14)-C(10)-C(9)	119	119	119	119	119	119	120	120	119	119	119
H(15)-C(11)-C(10)	119	119	119	119	119	119	119	119	120	120	120
C(16)-C(9)-C(8)	121	121	121	121	121	121	121	121	121	121	121
H(17)-C(16)-C(9)	111	111	111	111	111	111	111	111	112	112	112
H(18)-C(16)-C(9)	111	111	111	111	111	111	111	111	110	111	110
H(19)-C(16)-C(9)	111	111	111	111	111	111	111	111	110	109	110
H(20)-C(1)-C(2)	78	80	83	84	86	90	91	91	97	102	103
F(23)-B(22)-F(21)	91	91	91	92	92	92	93	96	107	107	107
F(24)-B(22)-F(21)	94	94	94	94	94	94	95	97	107	107	107
F(25)-B(22)-F(21)	94	94	94	94	94	95	95	97	112	112	111

Table 3. *The change in charges along the reaction interaction path of complex catalyst HF·BF_3 with p-methylstyrene.*

Atom	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C(1)	-0,202	-0,202	-0,205	-0,210	-0,216	-0,223	-0,233	-0,246	-0,257	-0,275
C(2)	-0,176	-0,177	-0,180	-0,181	-0,182	-0,181	-0,178	-0,170	-0,166	-0,150

H(3)	0,124	0,125	0,126	0,127	0,128	0,129	0,129	0,128	0,129	0,125
H(4)	0,122	0,123	0,124	0,126	0,128	0,129	0,131	0,133	0,135	0,138
H(5)	0,109	0,109	0,110	0,111	0,113	0,114	0,116	0,118	0,120	0,123
C(6)	-0,070	-0,076	-0,075	-0,073	-0,072	-0,071	-0,070	-0,070	-0,071	-0,074
C(7)	-0,066	-0,061	-0,059	-0,058	-0,056	-0,054	-0,052	-0,050	-0,048	-0,046
C(8)	-0,085	-0,083	-0,083	-0,083	-0,083	-0,083	-0,083	-0,082	-0,083	-0,083
C(9)	-0,123	-0,122	-0,122	-0,122	-0,122	-0,121	-0,121	-0,121	-0,120	-0,119
C(10)	-0,086	-0,086	-0,086	-0,086	-0,086	-0,086	-0,086	-0,086	-0,086	-0,086
C(11)	-0,062	-0,061	-0,061	-0,062	-0,062	-0,062	-0,062	-0,062	-0,061	-0,059
H(12)	0,110	0,107	0,108	0,108	0,108	0,108	0,108	0,106	0,107	0,104
H(13)	0,089	0,089	0,089	0,089	0,090	0,090	0,090	0,090	0,090	0,091
H(14)	0,088	0,088	0,088	0,088	0,088	0,088	0,089	0,089	0,089	0,090
H(15)	0,093	0,092	0,093	0,093	0,094	0,094	0,094	0,095	0,095	0,095
C(16)	-0,177	-0,177	-0,177	-0,177	-0,177	-0,177	-0,177	-0,177	-0,178	-0,178
H(17)	0,096	0,096	0,096	0,096	0,097	0,097	0,097	0,097	0,097	0,098
H(18)	0,109	0,111	0,111	0,110	0,111	0,111	0,111	0,111	0,111	0,112
H(19)	0,108	0,107	0,107	0,107	0,107	0,108	0,108	0,108	0,108	0,108
H(20)	0,343	0,344	0,345	0,347	0,349	0,352	0,356	0,361	0,367	0,374
F(21)	-0,331	-0,334	-0,336	-0,338	-0,341	-0,345	-0,349	-0,354	-0,359	-0,365
B(22)	0,809	0,806	0,806	0,807	0,808	0,809	0,810	0,810	0,811	0,809
F(23)	-0,286	-0,287	-0,288	-0,288	-0,289	-0,290	-0,291	-0,292	-0,293	-0,294
F(24)	-0,262	-0,264	-0,264	-0,264	-0,264	-0,264	-0,265	-0,266	-0,266	-0,268
F(25)	-0,272	-0,268	-0,269	-0,269	-0,269	-0,269	-0,269	-0,269	-0,270	-0,269

Continuation of ***Table 3.***

Atom	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
C(1)	-0,289	-0,304	-0,322	-0,331	-0,337	-0,354	-0,356	-0,364	-0,273	-0,252	-0,221
C(2)	-0,142	-0,131	-0,111	-0,102	-0,091	-0,068	-0,055	-0,027	0,120	0,122	0,114
H(3)	0,126	0,127	0,123	0,124	0,125	0,124	0,127	0,134	0,218	0,216	0,212
H(4)	0,139	0,141	0,143	0,144	0,145	0,148	0,149	0,152	0,164	0,153	0,139
H(5)	0,125	0,128	0,130	0,132	0,134	0,134	0,136	0,140	0,122	0,112	0,105
C(6)	-0,076	-0,080	-0,084	-0,088	-0,093	-0,097	-0,104	-0,119	-0,207	-0,210	-0,206
C(7)	-0,044	-0,042	-0,039	-0,038	-0,036	-0,034	-0,030	-0,021	0,068	0,068	0,069

C(8)	-0,083	-0,083	-0,085	-0,085	-0,085	-0,086	-0,086	-0,088	-0,116	-0,119	-0,118
C(9)	-0,119	-0,118	-0,117	-0,116	-0,115	-0,114	-0,113	-0,109	-0,055	-0,050	-0,050
C(10)	-0,086	-0,086	-0,086	-0,086	-0,087	-0,087	-0,088	-0,090	-0,112	-0,114	-0,115
C(11)	-0,058	-0,058	-0,053	-0,053	-0,052	-0,046	-0,044	-0,037	0,019	0,023	0,025
H(12)	0,104	0,105	0,102	0,102	0,103	0,102	0,103	0,107	0,185	0,185	0,183
H(13)	0,091	0,091	0,092	0,092	0,092	0,093	0,094	0,096	0,117	0,118	0,118
H(14)	0,090	0,090	0,090	0,091	0,091	0,092	0,093	0,095	0,110	0,110	0,110
H(15)	0,096	0,096	0,096	0,097	0,098	0,098	0,100	0,102	0,122	0,124	0,124
C(16)	-0,178	-0,178	-0,178	-0,178	-0,178	-0,178	-0,179	-0,179	-0,186	-0,186	-0,187
H(17)	0,098	0,098	0,099	0,099	0,099	0,099	0,099	0,101	0,117	0,118	0,118
H(18)	0,112	0,112	0,113	0,113	0,114	0,114	0,114	0,115	0,128	0,122	0,132
H(19)	0,108	0,108	0,108	0,108	0,109	0,111	0,112	0,113	0,132	0,140	0,128
H(20)	0,381	0,388	0,395	0,399	0,402	0,404	0,404	0,408	0,217	0,209	0,206
F(21)	-0,372	-0,379	-0,386	-0,395	-0,406	-0,415	-0,431	-0,454	-0,467	-0,467	-0,468
B(22)	0,811	0,812	0,812	0,814	0,817	0,817	0,823	0,835	0,847	0,846	0,848
F(23)	-0,295	-0,297	-0,297	-0,298	-0,301	-0,303	-0,308	-0,326	-0,453	-0,453	-0,453
F(24)	-0,269	-0,270	-0,273	-0,274	-0,276	-0,279	-0,283	-0,296	-0,444	-0,444	-0,444
F(25)	-0,270	-0,270	-0,270	-0,271	-0,272	-0,273	-0,276	-0,288	-0,372	-0,372	-0,371

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