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STUDY OF INTERACTION OF COMPLEX CATALYST $\text{BF}_3 \cdot \text{H}_2\text{O}$ WITH *p*-METHYLSTYRENE IN TOLUENE BY *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/water in toluene - with stoichiometric composition of mixture 1:1:1) by *ab initio* method was first performed. It was found that the activation energy of this reaction is 136 kJ/mol, and the thermal effect is 116 kJ/mol.

Keywords: *n*-methyl styrene, protonation, boron fluoride/ water catalyst, toluene, reaction heat, *ab initio* method.

Introduction

Until now, a number of important fundamental questions ~~remain~~ concerning the course of elementary acts of cationic polymerization of *p*-methylstyrene in the presence of a complex catalyst

which is often used in practice as an indifferent solvent, remain [1]. Therefore, the object of this work is to study the protonation procedure of *p*-methylstyrene in the presence of this complex catalyst.

Methodology

The protonation of cationic polymerization monomer of *p*-methylstyrene in the presence of a complex catalyst $\text{BF}_3 \cdot \text{H}_2\text{O}$ in toluene (with a stoichiometric composition of the mixture 1:1:1, respectively), was studied. The distance between the C(1) and H(20) atoms was chosen as the reaction coordinate. The calculation was performed using *ab initio* RHF/6-311G** quantum-chemical method [2] with geometry optimization for all parameters by the 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 (AC) [4]. The calculations were performed within the framework of molecular model and isolated molecule in toluene according to technique described in detail in [5] and applied in [6-19]. For visual molecular representation the MacMolPlt program was used [10].

Calculation data

The changes in bond lengths along the interaction coordinate, valence angles and atomic charges of molecular system during protonation reaction of *p*-methylstyrene in the presence of $\text{BF}_3 \cdot \text{H}_2\text{O}$ catalyst in toluene (the stoichiometric composition 1: 1: 1) are presented in Tables 1-3. Можно либо ед, либо множеств, в англ. Тоже можно так и так

Fig. 1 presents the geometric and electronic structure of initial model of *p*-methylstyrene, in Fig. 2 - the structure after interaction of catalyst with *p*-methylstyrene, Fig. 3 – the energy profile of this interaction, Fig. 4 – the changes in charges on atoms directly involved in interaction of complex catalyst $\text{BF}_3 \cdot \text{H}_2\text{O}$ with *p*-methylstyrene.

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 reaction coordinate.

At coordination stage (1st stage, steps 1-7), the charge on the C(1) atom changes from -0.219 to -0.254; at the stage of active center formation (2nd stage, steps 8-17) - from -0.266 to -0.358; at the stage of final product formation (3rd stage, steps 18-21) - from -0.361 to -0.262.

At 1st stage, the atomic charge on C (2) changes from -0,098 to -0,108; at 2nd stage - from 0,332 to 0,359; at 3rd stage - from -0,080 to 0,081.

At 1st stage, the atomic charge on H(20) changes from 0,325 to 0,329; at 2nd stage - from -0,104 to -0,100; at 3rd stage - from 0,360 to 0,213.

At 1st stage, the atomic charge on O(21) changes from -0,437 to -0,438; at 2nd stage - from -0,438 to -0,453; at 3rd stage - from -0,467 to -0,613.

At 1st stage, the atomic charge on B(23) changes from 0,820 to 0,818; at 2nd stage - from 0,819 to 0,794; at 3rd stage - from 0,790 to 0,809.

The charges on toluene atoms (C(27) -C(33) and H(33) -H(40)) along the reaction coordinate varied in the following ranges: for C(27) -C(33): from -0.176 to -0.119; for H(33)-H(40): from 0.139 to 0.123. During of reaction, the O(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 $[\text{BF}_3\cdot\text{OH}]$ is formed (Fig. 2).

The values of activation energy and thermal effect are calculated, equal to 136 kJ/mol and 116 kJ/mol, respectively.

Thus, the changes in atomic charges, behavior of reaction fragments, breaking and formation of new bonds in the reaction under study indicate that it proceeds according to the scheme of coordinated interactions.

Figure 1. The structure of initial model of complex catalyst $\text{BF}_3\cdot\text{H}_2\text{O}$ in toluene (at stoichiometric composition 1:1:1) with *p*-methylstyrene.

Figure 2. The final interaction structure of complex catalyst $\text{BF}_3 \cdot \text{H}_2\text{O}$ in toluene (at stoichiometric composition 1:1:1) with *p*-methylstyrene.

Figure 3. The total energy change (ΔE) of protonation (1-20 steps of interaction).

Figure 4. The change in charges along the reaction coordinate.

Table 1. The change in bond lengths as result of *p*-methylstyrene protonation using complex catalyst $BF_3 \cdot H_2O$ in toluene (stoichiometric composition 1:1:1)

[illegible]

[illegible]

C(33)-C(27)	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51	1,51
H(34)-C(28)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(35)-C(29)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(36)-C(30)	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07
H(37)-C(31)	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,07	1,08	1,07	1,07
H(38)-C(32)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(39)-C(33)	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08	1,08
H(40)-C(33)	1,08	1,08	1,08	1,08	1,08	1,09	1,09	1,09	1,09	1,09	1,09
H(41)-C(33)	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09	1,09

Table 2. The change in valence angles along the reaction coordinate of protonation interaction of *p*-methylstyrene, using complex catalyst $BF_3 \cdot H_2O$ in toluene (stoichiometric composition 1:1:1).

№ 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)	120	120	120	120	120	120	120	120	120	120
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	128	128
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)	119	119	119	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)	120	120	120	120	120	120	120	120	120	120
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	122	122	122
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)	88	88	87	87	87	84	85	85	82	84
O(21)-C(2)-C(1)	77	76	77	76	76	76	75	74	74	72

[illegible]

Continuation of Table 2.

[illegible]

H(13)-C(8)-C(7)	119	119	119	119	119	119	119	119	120	121	121
H(14)-C(10)-C(9)	120	120	120	120	120	120	120	120	120	120	120
H(15)-C(11)-C(10)	119	119	119	119	119	119	119	119	119	120	120
C(16)-C(9)-C(8)	122	122	122	122	122	122	122	122	121	119	119
H(17)-C(16)-C(9)	111	111	111	111	111	111	111	111	111	109	109
H(18)-C(16)-C(9)	111	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	112	112
H(20)-C(1)-C(2)	84	86	87	89	91	94	96	97	96	103	105
O(21)-C(2)-C(1)	70	68	65	61	60	56	54	52	52	67	66
H(22)-O(21)-C(2)	86	87	87	92	92	92	92	93	94	138	137
B(23)-O(21)-C(2)	126	127	128	127	128	127	128	128	126	110	110
F(24)-B(23)-O(21)	103	103	104	103	104	103	104	105	105	111	111
F(25)-B(23)-O(21)	103	103	104	104	104	104	105	105	106	107	107
F(26)-B(23)-O(21)	101	101	101	102	102	103	103	104	105	112	112
C(28)-C(27)-C(1)	89	89	89	90	90	87	87	88	88	87	87
C(29)-C(28)-C(27)	121	121	121	121	121	121	121	121	121	121	121
C(30)-C(29)-C(28)	120	120	120	120	120	120	120	120	120	120	120
C(31)-C(30)-C(29)	119	119	119	119	119	119	119	119	119	119	119
C(32)-C(31)-C(30)	120	120	120	120	120	120	120	120	120	120	120
C(33)-C(27)-C(1)	121	121	121	125	125	128	128	128	128	132	132
H(34)-C(28)-C(27)	120	120	120	120	120	120	120	120	120	120	120
H(35)-C(29)-C(28)	120	120	120	120	120	120	120	120	120	120	120
H(36)-C(30)-C(29)	121	121	121	121	121	121	121	121	121	121	121
H(37)-C(31)-C(30)	120	120	120	120	120	120	120	120	120	119	119
H(38)-C(32)-C(31)	119	119	119	119	119	119	119	119	119	119	119
H(39)-C(33)-C(27)	111	111	111	111	111	111	111	111	111	111	111
H(40)-C(33)-C(27)	111	111	111	111	111	111	111	111	111	111	111
H(41)-C(33)-C(27)	111	111	111	111	111	111	111	111	111	111	111

Table 3. The change in charges along the reaction interaction path of complex catalyst $\text{BF}_3 \cdot \text{H}_2\text{O}$ in toluene (stoichiometric composition 1:1:1) with *p*-methylstyrene.

Atom	1	2	3	4	5	6	7	8	9	10
C(1)	-0,219	-0,224	-0,226	-0,233	-0,241	-0,241	-0,254	-0,266	-0,262	-0,282

C(2)	-0,098	-0,097	-0,101	-0,100	-0,098	-0,111	-0,108	-0,104	-0,137	-0,125
H(3)	0,100	0,100	0,101	0,102	0,103	0,102	0,103	0,104	0,105	0,106
H(4)	0,120	0,121	0,123	0,125	0,126	0,132	0,133	0,135	0,144	0,145
H(5)	0,135	0,136	0,136	0,139	0,141	0,140	0,144	0,148	0,146	0,152
C(6)	-0,130	-0,132	-0,139	-0,140	-0,143	-0,127	-0,130	-0,134	-0,103	-0,109
C(7)	-0,060	-0,060	-0,060	-0,059	-0,059	-0,054	-0,054	-0,054	-0,048	-0,048
C(8)	-0,077	-0,077	-0,076	-0,076	-0,076	-0,078	-0,079	-0,079	-0,082	-0,082
C(9)	-0,124	-0,124	-0,126	-0,126	-0,126	-0,125	-0,125	-0,125	-0,122	-0,122
C(10)	-0,060	-0,060	-0,062	-0,062	-0,062	-0,070	-0,070	-0,070	-0,080	-0,080
C(11)	-0,143	-0,140	-0,123	-0,119	-0,114	-0,112	-0,104	-0,100	-0,104	-0,096
H(12)	0,093	0,093	0,093	0,093	0,094	0,094	0,094	0,094	0,094	0,094
H(13)	0,092	0,092	0,092	0,092	0,092	0,092	0,092	0,092	0,092	0,092
H(14)	0,101	0,101	0,100	0,100	0,100	0,100	0,100	0,100	0,098	0,098
H(15)	0,119	0,119	0,116	0,116	0,116	0,117	0,117	0,117	0,124	0,123
C(16)	-0,175	-0,175	-0,175	-0,175	-0,176	-0,176	-0,176	-0,176	-0,176	-0,176
H(17)	0,095	0,095	0,095	0,095	0,096	0,096	0,096	0,096	0,097	0,097
H(18)	0,112	0,112	0,112	0,112	0,112	0,113	0,113	0,114	0,115	0,115
H(19)	0,116	0,116	0,116	0,116	0,116	0,113	0,114	0,114	0,110	0,111
H(20)	0,325	0,326	0,325	0,326	0,328	0,326	0,329	0,332	0,335	0,341
O(21)	-0,437	-0,437	-0,436	-0,437	-0,436	-0,437	-0,438	-0,438	-0,439	-0,441
H(22)	0,336	0,334	0,332	0,331	0,329	0,324	0,323	0,322	0,315	0,314
B(23)	0,820	0,822	0,819	0,821	0,822	0,817	0,818	0,819	0,810	0,810
F(24)	-0,340	-0,339	-0,339	-0,338	-0,337	-0,335	-0,334	-0,334	-0,332	-0,333
F(25)	-0,360	-0,360	-0,359	-0,359	-0,360	-0,356	-0,357	-0,358	-0,354	-0,356
F(26)	-0,340	-0,341	-0,340	-0,341	-0,343	-0,339	-0,342	-0,344	-0,339	-0,342
C(27)	-0,123	-0,124	-0,124	-0,124	-0,125	-0,123	-0,124	-0,124	-0,121	-0,121
C(28)	-0,092	-0,093	-0,094	-0,094	-0,094	-0,097	-0,097	-0,097	-0,098	-0,098
C(29)	-0,077	-0,080	-0,078	-0,081	-0,083	-0,081	-0,082	-0,084	-0,085	-0,086
C(30)	-0,176	-0,166	-0,169	-0,158	-0,149	-0,148	-0,141	-0,135	-0,131	-0,128
C(31)	-0,112	-0,116	-0,110	-0,112	-0,116	-0,107	-0,109	-0,111	-0,102	-0,103
C(32)	-0,084	-0,084	-0,087	-0,088	-0,089	-0,095	-0,095	-0,096	-0,102	-0,102
C(33)	-0,178	-0,178	-0,177	-0,177	-0,177	-0,176	-0,176	-0,176	-0,176	-0,176
H(34)	0,089	0,088	0,088	0,088	0,087	0,086	0,086	0,086	0,085	0,085

H(35)	0,100	0,099	0,099	0,098	0,098	0,096	0,096	0,096	0,094	0,094
H(36)	0,122	0,120	0,124	0,122	0,121	0,121	0,120	0,118	0,116	0,115
H(37)	0,129	0,129	0,126	0,125	0,125	0,124	0,123	0,123	0,121	0,121
H(38)	0,092	0,092	0,091	0,091	0,090	0,089	0,089	0,088	0,087	0,087
H(39)	0,100	0,100	0,099	0,099	0,098	0,098	0,098	0,097	0,096	0,096
H(40)	0,096	0,096	0,096	0,096	0,096	0,096	0,096	0,095	0,096	0,096
H(41)	0,115	0,115	0,115	0,115	0,114	0,114	0,114	0,114	0,113	0,113
C(1)	-0,292	-0,310	-0,325	-0,334	-0,341	-0,354	-0,358	-0,361	-0,364	-0,285
C(2)	-0,133	-0,123	-0,115	-0,127	-0,120	-0,113	-0,100	-0,080	-0,042	0,089
H(3)	0,108	0,109	0,110	0,112	0,114	0,115	0,117	0,121	0,128	0,144
H(4)	0,152	0,154	0,157	0,166	0,169	0,178	0,180	0,182	0,181	0,140
H(5)	0,153	0,158	0,163	0,164	0,168	0,171	0,175	0,181	0,187	0,175
C(6)	-0,102	-0,106	-0,110	-0,087	-0,094	-0,091	-0,100	-0,112	-0,131	-0,204

Continuation of Table 3.

Atom	11	12	13	14	15	16	17	18	19	20	21
C(7)	-0,047	-0,046	-0,044	-0,044	-0,042	-0,042	-0,038	-0,034	-0,025	0,032	0,034
C(8)	-0,083	-0,083	-0,084	-0,085	-0,085	-0,086	-0,087	-0,089	-0,092	-0,127	-0,128
C(9)	-0,122	-0,121	-0,120	-0,118	-0,117	-0,115	-0,113	-0,110	-0,102	-0,039	-0,036
C(10)	-0,084	-0,084	-0,084	-0,089	-0,089	-0,091	-0,092	-0,094	-0,099	-0,137	-0,138
C(11)	-0,087	-0,084	-0,080	-0,083	-0,078	-0,069	-0,064	-0,056	-0,042	0,114	0,118
H(12)	0,094	0,094	0,094	0,094	0,094	0,094	0,095	0,097	0,100	0,117	0,118
H(13)	0,091	0,092	0,092	0,092	0,092	0,092	0,093	0,094	0,097	0,110	0,110
H(14)	0,098	0,098	0,098	0,097	0,098	0,098	0,099	0,101	0,104	0,123	0,124
H(15)	0,124	0,124	0,124	0,129	0,130	0,130	0,133	0,138	0,151	0,216	0,218
C(16)	-0,176	-0,176	-0,177	-0,177	-0,177	-0,177	-0,178	-0,178	-0,179	-0,188	-0,188
H(17)	0,096	0,097	0,097	0,097	0,097	0,097	0,098	0,098	0,100	0,140	0,140
H(18)	0,114	0,114	0,114	0,115	0,115	0,114	0,115	0,116	0,118	0,122	0,123
H(19)	0,112	0,112	0,112	0,111	0,112	0,113	0,114	0,116	0,119	0,122	0,123
H(20)	0,347	0,353	0,360	0,359	0,361	0,359	0,359	0,360	0,369	0,224	0,213
O(21)	-0,442	-0,444	-0,447	-0,445	-0,447	-0,447	-0,453	-0,467	-0,508	-0,614	-0,613
H(22)	0,311	0,310	0,309	0,306	0,305	0,302	0,300	0,296	0,290	0,244	0,243
B(23)	0,805	0,805	0,804	0,800	0,798	0,797	0,794	0,790	0,787	0,810	0,809

F(24)	-0,334	-0,335	-0,337	-0,342	-0,344	-0,350	-0,355	-0,361	-0,373	-0,440	-0,439
F(25)	-0,356	-0,358	-0,360	-0,362	-0,366	-0,369	-0,375	-0,383	-0,399	-0,466	-0,467
F(26)	-0,341	-0,343	-0,346	-0,344	-0,347	-0,347	-0,352	-0,358	-0,368	-0,408	-0,408
C(27)	-0,120	-0,120	-0,120	-0,120	-0,120	-0,120	-0,120	-0,120	-0,120	-0,122	-0,122
C(28)	-0,097	-0,098	-0,098	-0,097	-0,097	-0,095	-0,096	-0,096	-0,097	-0,099	-0,099
C(29)	-0,087	-0,087	-0,088	-0,087	-0,087	-0,087	-0,088	-0,089	-0,090	-0,088	-0,088
C(30)	-0,124	-0,122	-0,120	-0,121	-0,119	-0,122	-0,120	-0,119	-0,118	-0,131	-0,130
C(31)	-0,101	-0,102	-0,103	-0,107	-0,107	-0,110	-0,110	-0,110	-0,111	-0,104	-0,105
C(32)	-0,104	-0,104	-0,104	-0,102	-0,102	-0,101	-0,101	-0,102	-0,104	-0,106	-0,106
C(33)	-0,176	-0,176	-0,176	-0,177	-0,177	-0,177	-0,176	-0,176	-0,176	-0,176	-0,176
H(34)	0,084	0,084	0,084	0,084	0,084	0,084	0,084	0,084	0,083	0,079	0,079
H(35)	0,093	0,093	0,092	0,092	0,092	0,092	0,092	0,092	0,091	0,089	0,089
H(36)	0,113	0,113	0,112	0,109	0,109	0,110	0,110	0,111	0,112	0,126	0,126
H(37)	0,120	0,121	0,121	0,124	0,125	0,126	0,126	0,128	0,131	0,139	0,139
H(38)	0,087	0,087	0,087	0,087	0,087	0,087	0,087	0,087	0,087	0,083	0,083
H(39)	0,095	0,095	0,095	0,095	0,095	0,093	0,093	0,093	0,092	0,090	0,090
H(40)	0,097	0,097	0,097	0,097	0,097	0,099	0,099	0,099	0,098	0,094	0,094
H(41)	0,113	0,113	0,112	0,112	0,112	0,112	0,112	0,112	0,112	0,111	0,110

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