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Ab initio Study of Radical-Molecule Reaction: $F+CH_2CHCH_3$

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The radical-molecule reaction F +propene (CH_2CHCH_3) was studied in detail by using the Becke's three parameter Lee-Yang-Parr-B3LYP/6-311G(d,p) and coupled cluster with single, double, and triple excitations-CCSD(T)/6-311+G(2d,2p). It is shown that F +propene reaction mainly occurs through complex-formation mechanism: F attacks the double bond of propene leading to the formation of complex 1 and complex 2. As the two radical complexes are metastable, they can quickly dissociate to $H+C_3H_5F$, $CH_3+C_2H_3F$ and $HF+C_3H_5$. Based on the *ab initio* calculations, the $CH_3+C_2H_3F$ is the main channel, and the H elimination and HF forming channels also provide some contribution to products. The calculated values are in good agreement with the recently reported experimental results.

Key words: F , Propene, Complex-formation mechanism, Abstraction mechanism, Barrier height

I. INTRODUCTION

The reactivity of the fluorine atom is an interesting research topic because of the complicated nature of the reaction mechanism involved in these reactions and its importance in the etching processes [1-7]. Theoretically, the benchmark $F+H_2$ reaction has been widely studied [8-12], including its potential energy surface properties and dynamics. Theoretical investigations were also carried out for F atom reaction with methane [13-15]. Recently, the crossed molecular beam investigation of the F +propene reaction has been performed by Ran *et al.* [16].

This experiment aims to further look systematically at the reaction dynamics of F atom with hydrocarbon molecules with both single and double/triple bonds, in which reactions through both direct abstraction and long-lived complex formation mechanisms are probable. Three different reaction channels, $H+C_3H_5F$, $CH_3+C_2H_3F$ and $HF+C_3H_5$, have been observed. The formation of CH_3 was found to be the most important reaction pathway for the title reaction, while both H and HF formation channels are also significant. From the experimental observation, it is not clear how the reaction mechanism is in detail. To our knowledge, however, no theoretical study of the mechanism for the F +propene has been reported so far. In this work, we apply the *ab initio* approach to study the F +propene reaction. We use high level *ab initio* methods to compute the reaction potential energy surface (PES). The *ab initio* results are then employed to analyze the reaction mechanism and to give qualitative conclusion about product branching ratios.

II. COMPUTATIONAL DETAILS

The geometry of equilibrium structures and transition states of various species has been optimized by the hybrid density functional B3LYP method [17,18] with the 6-311G(d,p) basis set. Vibrational frequencies calculated at the B3LYP/6-311G(d,p) level were used for characterization of the stationary points and zero-point energy (ZPE) corrections. To obtain more accurate energies on the PES, we employed the CCSD(T) [19] method with the large 6-311+G(2d,2p) basis set. The CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311G(d,p)+ZPE (B3LYP/6-311G(d,p)) calculational scheme [20] has been shown to provide accuracies of 1-2 kJ/mol for atomization energies of the G2 test set of molecules. Such accuracy is also expected for other molecules, unless their wave functions exhibit a strong multireference character. A similar CCSD(T)//B3LYP approach has also been demonstrated to be accurate for transition state energies [21]. All the calculations were carried out using the GAUSSIAN 03 program package [22].

III. RESULTS AND DISCUSSION

Table I presents total and relative energies for various species, while their unscaled vibrational frequencies are collected in Table II. Figure 1 showed optimized geometries and their parameters of various stationary structures for the F +propene reaction in Fig.2. Profile of the ground PES is depicted in Fig.3.

According to our calculations, the F +propene reaction in the ground electronic state produces two long-lived intermediates: complex 1 ($CH_2FC\cdot HCH_3$) ("·" denotes an unpaired single electron) and complex 2 ($C\cdot H_2CHFCH_3$) without entrance barriers. From Fig.3, it is seen that complex 1 and complex 2 reside

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TABLE I Total energies (hartrees) and relative energies (kJ/mol) for various species calculated at the CCSD(T)/6-311+G(2d,2p) level of theory

Species	Total energy	Relative energy	Species	Total energy	Relative energy
F+CH ₂ CHCH ₃	-217.146031	0	TS7	-217.16976	-62.3
Complex 1	-217.21246	-174.7	<i>t</i> -CHFCHCH ₃ +H	-217.16074	-38.5
Complex 2	-217.21532	-181.8	<i>c</i> -CHFCHCH ₃ +H	-217.16152	-40.5
TS1	-217.15416	-21.3	CH ₂ CHCH ₂ F+H	-217.15675	-28.0
TS2	-217.15280	-18.0	C·HCHCH ₃ +HF	-217.18342	-98.2
TS3	-217.14891	-7.5	CH ₂ CFCH ₃ +H	-217.16804	-57.7
TS4	-217.15719	-29.3	CH ₂ CHF+CH ₃	-217.17927	-87.4
TS5	-217.16285	-44.3	CH ₂ C·CH ₃ +HF	-217.22920	-218.2
TS6	-217.12248	-61.9			

TABLE II Vibrational frequencies for various species and transition states calculated at the B3LYP/6-311G(d,p) level of theory

Species	Frequencies/cm ⁻¹	Species	Frequencies/cm ⁻¹
CH ₂ CHCH ₃ (C ₁ , ¹ A)	204, 425, 591, 923, 941, 948, 1029, 1070, 1189, 1327, 1408, 1448, 1480, 1494, 1712, 3012, 3056, 3091, 3120, 3127, 3208,	TS5 (C ₁ , ² A)	504 <i>i</i> , 101, 184, 272, 460, 526, 551, 598, 780, 852, 915, 950, 1148, 1285, 1398, 1415, 1421, 1564, 3083, 3160, 3189, 3241, 3248, 3261
Complex 1 (C ₁ , ² A)	70, 94, 253, 352, 562, 880, 923,966, 1004, 1117, 1148, 1256, 1377, 1392, 1416, 1473, 1486, 1488, 2944, 2952, 3053, 3060, 3102, 3175	TS6 (C ₁ , ² A)	475 <i>i</i> , 102, 162, 213, 443, 476, 804, 910, 930, 947, 1048, 1168, 1223, 1394, 1417, 1466, 1485, 1634, 2409, 3024, 3084, 3098, 3119, 3219
Complex 2 (C ₁ , ² A)	65, 239, 347, 383, 456, 627, 820, 897, 930, 1052, 1160, 1184, 1340, 1379, 1417, 1460, 1485, 1497, 3031, 3035, 3103, 3113, 3136, 3245	TS7 (C ₁ , ² A)	256 <i>i</i> , 161, 199, 340, 421, 611, 909, 919, 943, 954, 1045, 1201, 1311, 1404, 1439, 1472, 1488, 1621, 3019, 3079, 3117, 3158, 3171, 3257
TS1 (C ₁ , ² A)	591 <i>i</i> , 129, 239, 258, 363, 496, 675, 773, 926, 946, 1020, 1055, 1144, 1261, 1386, 1423, 1485, 1488, 1660, 3018, 3061, 3124, 3169, 3211	<i>t</i> -CHFCHCH ₃ (C ₁ , ¹ A)	207, 286, 290, 532, 821,930,949, 1066, 1111, 1150, 1285, 1336, 1421, 1481, 1496, 1745, 3018, 3063, 3093, 3160, 3186
TS2 (C ₁ , ² A)	304 <i>i</i> , 98, 171, 243, 334, 447, 673,926, 964, 985, 1021, 1031, 1177, 1263, 1309, 1392, 1459, 1497, 1676, 3023, 3078, 3133, 3151, 3221	<i>c</i> -CHFCHCH ₃ (C ₁ , ¹ A)	141, 248, 438, 678,767, 928,938, 1018, 1065, 1140, 1269, 1387, 1425, 1490, 1491, 1743, 3022, 3064, 3121, 3164, 3209
TS3 (C ₁ , ² A)	578 <i>i</i> , 102, 192, 207, 319, 454, 776,888, 928, 961, 1054, 1152, 1299, 1308, 1402, 1472, 1479, 1631, 2133, 3016, 3066, 3109, 3142, 3171	CH ₂ CHCH ₂ F (C ₁ , ¹ A)	118, 327, 436,654, 928, 966, 986, 1027, 1036, 1178, 1262, 1315, 1395, 1461, 1498, 1713, 3025, 3078, 3128, 3146, 3214
TS4 (C ₁ , ² A)	802 <i>i</i> , 213, 367, 428, 467, 526, 533, 691, 842, 853, 949, 1022, 1062, 1278, 1397, 1426, 1470, 1488, 1637, 3036, 3103, 3136, 3168, 3267	C·HCHCH ₃ (C ₁ , ² A)	194, 408, 612, 790, 813, 931, 1061, 1105, 1271, 1403, 1484, 1485, 1684, 3006, 3020, 3067, 3115, 3240
CH ₂ CHF (C ₁ , ¹ A)	484, 731, 887, 936, 969, 1166, 1330, 1412, 1713, 3161, 3196, 3257	CH ₂ CFCH ₃ (C ₁ , ¹ A)	199, 391, 470, 484, 751, 851, 873, 952, 1025, 1072, 1278, 1405, 1429, 1469, 1488, 1745, 3030, 3080, 3129, 3167, 3259
		CH ₂ C·CH ₃ (C ₁ , ² A)	184, 315, 477, 882, 897, 935, 1051, 1099, 1392, 1416, 1456, 1473, 1747, 2960, 3023, 3048, 3072, 3143

in deep wells, 174.3 and 181.8 kJ/mol below the reactants at the CCSD(T)/6-311+G(2d,2p)//B3LYP/6-311G(d,p) level. These two complexes can easily isomerize to each other via TS7 with a barrier of 112.0

and 119.5 kJ/mol in the forward and reverse directions, respectively.

Three pathways lead from complex 1 to various de-

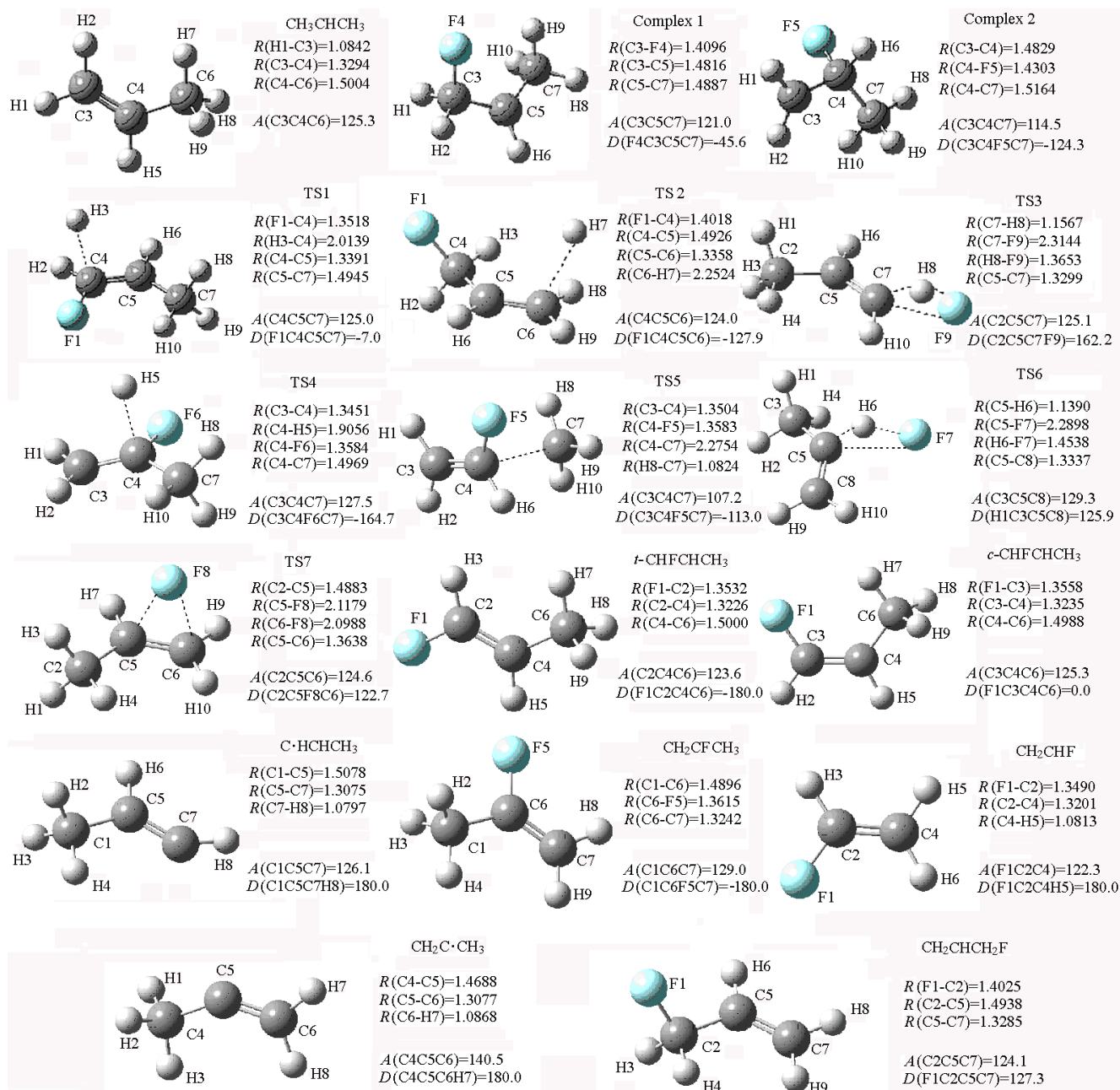


FIG. 1 Optimized geometries of stationary points calculated at the B3LYP/6-311G(d,p) level of theory; Optimized geometric parameters (distances R in Å, angles A and D in $^\circ$) of various stationary structures for the F+propene reaction.

composition products, corresponding to t -CHFCHCH₃+H, CH₂CHCH₂F+H and C-HCHCH₃+HF. It is shown in the above scheme. The first channel occurs via TS1 by H elimination with a barrier of 153.0 and 17.1 kJ/mol in the forward and reverse directions, respectively; the reverse reaction has a low barrier and can easily associate back to complex 1. The t -CHFCHCH₃+H product channel is 38.5 kJ/mol exothermic with respect to F+propene. t -CHFCHCH₃ has one isomer: c -CHFCHCH₃, which is a little more stable than t -CHFCHCH₃ by 2.09 kJ/mol. The second

channel occurs via TS2 by H elimination, and the forward and reverse barriers are 156.3 and 10.0 kJ/mol. The CH₂CHCH₂F+H product channel is 28.0 kJ/mol exothermic with respect to F+propene and these two products can also easily combine back to complex 1 as having a rather low reverse barrier. The last channel occurs via TS3 by 1,1-HF elimination with a barrier of 166.8 and 90.7 kJ/mol in the forward and reverse directions, respectively. C-HCHCH₃+HF product channel is 98.2 kJ/mol exothermic with respect to F+propene. As the barrier heights for the three product channels

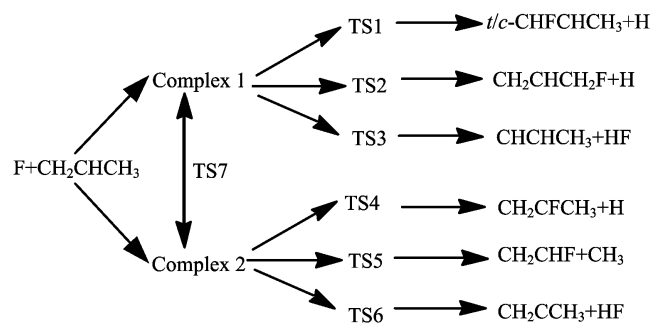


FIG. 2 The F+propene reaction in the ground electronic state.

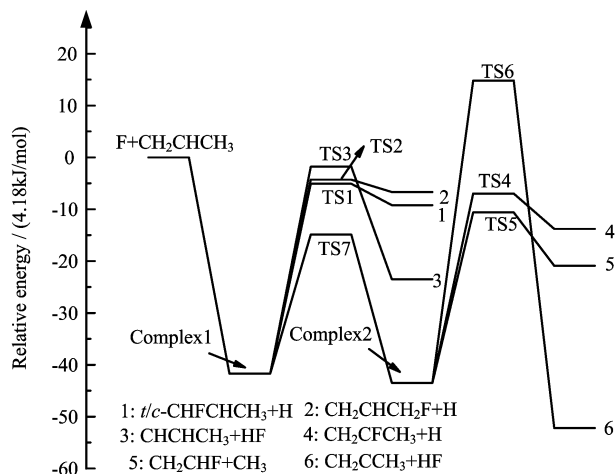


FIG. 3 Potential energy diagram constructed using the CCSD(T)/6-311+G(2d,2p) method for the F+propene reaction.

are similar, we can anticipate that C-HCHCH₃+HF channel is more stable than two H-elimination channels based on the exothermicities and this channel will significantly contribute to products.

In contrast, complex 2 can also dissociate to various products via three reaction channels, which lead to CH₂CFCH₃+H, CH₂CHF+CH₃ and CH₂C·CH₃+HF, respectively. H-elimination channel proceeds via TS4 and its forward and reverse barriers are 152.6 and 28.4 kJ/mol, respectively. This channel is 57.7 kJ/mol exothermic with respect to reactants. CH₃-elimination channel proceeds via TS5 by C4-C7 bond cleavage with a barrier of 137.5 and 43.1 kJ/mol in the forward and reverse directions, respectively. CH₃-elimination channel's exothermicity is 87.4 kJ/mol with respect to reactants. HF-formation channel proceeds via TS6 and its exothermicity is 218.2 kJ/mol; its forward and reverse barriers are 243.7 and 280.1 kJ/mol, respectively.

Based on the above analysis, we can see H-elimination most likely occurs at C3 and C7 sites of complex 1 (see Fig.1 for atom notations), H-elimination of C5 site will lead to extremely unstable triplet CH₂FC:CH₃ ("·" denotes the two unpaired single electron), which is spin-

forbidden unless CH₂FC:CH₃ transforms to singlet isomer. For complex 2, the H-elimination most likely occurs at C4 site. The other two sites' H-elimination will give triplet products and these processes are also spin-forbidden.

CH₃ elimination most likely occurs at C4 site of complex 2; while CH₃ elimination occurring at C5 site of complex 1 will produce triplet CH₂FC:H, which is spin-forbidden unless CH₂FC:H isomerizes to singlet one.

According to the experimental results, it is quite clear that the HF formation channel shows a clear forward scattering angular distribution, indicating that this reaction channel likely takes place through a large impact pickup type mechanism. However, a careful search of a transition state for this process was not successful; the calculations converged to TS3 or TS6, and we conclude that the HF abstraction reaction may occur in the first excited state, as recently demonstrated for the O(¹D)+SiH₄ reaction [23]; or for this channel there is no distinct transition state like some barrierless bond cleavage reactions [24]. Alternatively, the forward-scattered products can be formed on the ground-state PES through the trajectories that bypass the long-lived CH₂FC·HCH₃ and C·H₂CHFCH₃ intermediates and lead to the HF product via short-lived CH₂FC·HCH₃ and C·H₂CHFCH₃ complex. This dynamics possibility has been recently demonstrated for the O(¹D)+CH₄→OH+CH₃ reaction by quasi-classical trajectory (QCT) calculations of Sayos *et al.* [25] and direct *ab initio* dynamics simulations of Yu and Muckerman [26]. Both studies consistently show that, even if only the ground electronic state trajectories are considered, the differential cross section for the direct reaction exhibits a pronounced forward peak superimposed on a relatively isotropic background. According to our theoretical calculations, HF formation channel can also proceed by long-lived complex formation via TS3 and TS6 except pickup mechanism. The channel via TS6 can lead to the HF formation only at collision energies higher than 61.9 kJ/mol, unless quantum mechanical tunneling occurs through the barrier at TS6. It is not likely to occur in experimental conditions (collision energy 21.7 kJ/mol).

According to energy conservation, we can expect that CHCHCH₃+HF and CH₂CHF+CH₃ are the main product channels. Their exothermicities are 98.2 and 87.4 kJ/mol, respectively. One of key factors that affect product's branching ratios is barrier height. On the basis of the computed barrier heights of the six product channels, the barrier height of CH₃ elimination (137.5 kJ/mol) is the lowest in the all product channels. So it is inferred that CH₃ elimination is the main channel, which consists with the experimental results [16]. The barrier of HF formation (166.8 kJ/mol) is the highest one among all the product channels. The barrier heights of H elimination (153.0, 156.3 and 152.6 kJ/mol) are between the values of above two channels. It needs further dynamic calculations in order

to compare product branching ratios with experimental ones [16].

IV. CONCLUSION

The F+propene reaction involving long-lived complexes has been studied employing the *ab initio* approaches. Three product channels have been calculated in this reaction: H+C₃H₅F, CH₃+C₂H₃F and HF+C₃H₅. H elimination can occur at C3 and C7 sites of CH₂FC·HCH₃, C4 site of C·H₂CHFCH₃; CH₃ elimination can occur at C4 site of C·H₂CHFCH₃; HF formation can occur through long-lived complex formation mechanism by CH₂FC·HCH₃ and C·H₂CHFCH₃ via TS3 and TS6, or through pickup mechanism on first excited PES. Based on the computed barrier heights and products' exothermicities, it is concluded that CH₃ elimination is the main channel, H and HF elimination channels also significantly contribute to products. This conclusion consists with the experimental results [16].

V. ACKNOWLEDGMENTS

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