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Theoretical Studies on the Dynamics of the Fluorine Atom Reaction with *trans*-1,3-butadiene

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Theoretical studies of F atom reaction with *trans*-1,3-butadiene were carried out at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) levels. Energies and structures for all reactants, products and transition states were determined. Two reaction pathways involving the formation of the complexes $CH_2CHCHFCH_2$ and $CH_2CHCHCH_2F$ were found in this reaction. Theoretical results suggest that the H atom channel observed in previous crossed beam experiment occurs likely via these two long-lived complex formation pathways. For the complex $CH_2CHCHFCH_2$ pathway, another reaction channel ($C_2H_3+C_2H_3F$) is also accessible. Relative importance of the $C_2H_3+C_2H_3F$ channel versus the H formation channel via the same reaction pathway has also been estimated, suggesting that it would be difficult to observe the $C_2H_3+C_2H_3F$ channel in a crossed molecular beam experiment. Theoretical analysis also shows that the HF formation proceeds via direct abstraction mechanisms, though it is likely a minor process in this reaction.

Key words: Reaction dynamics, Fluorine atom, Reaction mechanism

I. INTRODUCTION

Olefin molecules represent an important class of organic compounds which play an important role in our daily life and industrial processes because the activation of their π-bond can induce numbers of significant chemical reactions, including addition, polymerization and oxidation etc. In addition, 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. The F atom reactions with olefins and several small molecules have been investigated extensively [1-9]. In this work, a variety of approaches have been used to test the random lifetime assumption of the RRKM theory of unimolecular decomposition, which requires the available energy fully randomized among all internal degrees of freedom in the transition state. The formation of long-lived complex was found to be important in the F atom reaction with the olefins.

As the simplest conjugated polyenes, 1,3-butadiene is the subject of experimental and theoretical studies [10-12]. Neumark and coworkers investigated the photodissociation dynamics of the 1,3-butadiene and its isotopic species at 193 nm using the tunable VUV synchrotron based on photoionization sampling technique [13]. Mebel *et al.* also investigated the photodissociation mechanism using the *ab initio* method [14]. Recently, Gu *et al.* studied the F atom reaction with 1,3-butadiene using the crossed molecular beam technique [15]. Only the H atom formation channel has been reported. From the product angular distribution measurement, the H atom formation channel is likely from a complex formation pathway. It is not known, however, which complex formation pathway is responsible for this channel. In addition, it is not clear whether other minor reaction channels are also present. It is, therefore, necessary to investigate this reaction from the theoretical point of view to clarify these points.

In this paper, we report a theoretical study on the energetics and the dynamics of the F-atom reaction with *trans*-1,3-butadiene using the high level *ab initio* method. Since the trans-structure of 1,3-butadiene is more stable than its *cis*-structure for about 8.4 kJ/mol, only the reaction of F atom with the *trans*-1,3-butadiene is considered in this work. The energies and structures of reactants, products and transition states were calculated using high level *ab initio* methods. In the next sections, a brief description of the theoretical methods will be provided and followed by the presentation of the theoretical results. Finally, a conclusion is drawn from these studies.

II. THEORETICAL METHODS

The geometries for all species involved in the title reaction have been optimized by employing the hybrid density functional B3LYP method with the 6-311G(d,p) basis set [16]. 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. For comparison at transition states, we also used the MP2/6-311G(d,p) approach for geometry optimization and vibrational frequencies calcula-

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TABLE I Relative energy and zero point energy correction (ZPE) of reactants, products, intermediates and transition states for the F atom reaction with *trans*-1,3-butadiene

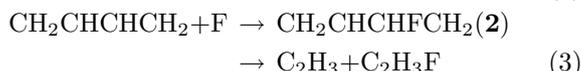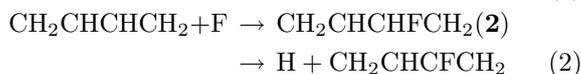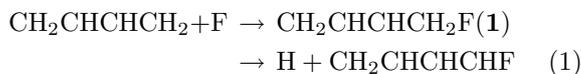| Species	ZPE/(kJ/mol)	Relative energy/(kJ/mol)	
		B3LYP/6-311G**	CCSD(T)/6-311G**
$F+C_4H_6$	247.0	0.0	0.0
$H+CH_2CHCHCHF$	203.6	−48.5	−33.9
$HF+CH_2CHCHCH$	186.0	−80.3	−65.6
$H+CH_2CHCFCH_2$	202.3	−55.2	−44.3
$HF+CH_2CHCCH_2$	207.7	−140.9	−114.5
$C_2H_3+C_2H_3F$	209.8	−44.7	−15.0
$CH_2CHCHCH_2F(\mathbf{1})$	229.1	−230.7	−201.5
$CH_2CHCHFCH_2(\mathbf{2})$	224.0	−168.9	−153.4
TS1	214.0	−32.6	5.4
TS2	215.3	−20.5	11.3
TS3	224.0	−13.0	24.7
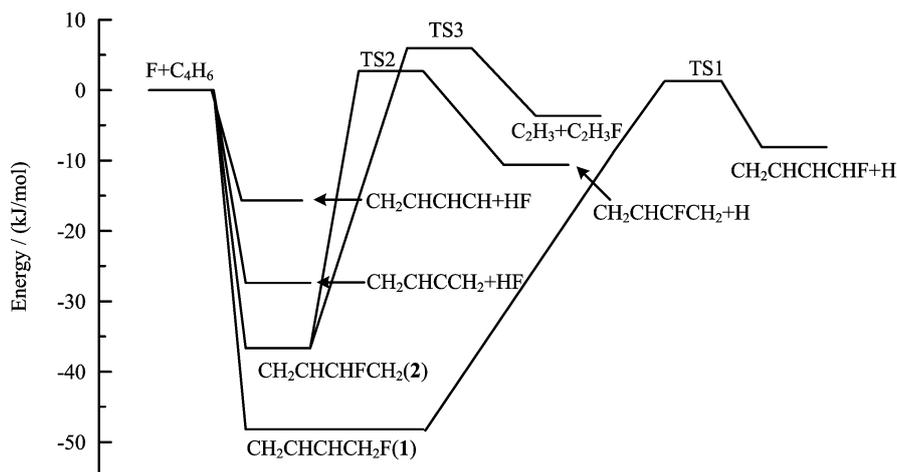
FIG. 1 The potential energy diagram for the F atom reaction with *trans*-1,3-butadiene.

tions [17]. The numbers of imaginary frequencies for intermediates and transition states are 0 and 1 respectively. The zero-point energy and frequencies calculated at the level B3LYP/6-311G(d,p) are used without scaling. To obtain more accurate energies on the PES, we employed the CCSD(T) method with the 6-311G(d,p) basis set to calculate the single-point energy based on the geometries of the B3LYP/6-311G(d,p) level [18]. All the energies quoted and discussed in the present article have already included the ZPE correction. All calculations shown here have been carried out using the Gaussian 03 program on a powerful PC [19].

III. RESULTS AND DISCUSSION

Figure 1 shows the whole potential energy surfaces for the F-atom reaction with *trans*-1,3-butadiene obtained at the CCSD(T)/6-311g(d,p) level. Total five reaction pathways are energetically accessible,

$$CH_2CHCHCH_2+F \rightarrow CH_2CHCHCH_2F(\mathbf{1})$$
$$\rightarrow H + CH_2CHCHCHF \quad (1)$$
$$CH_2CHCHCH_2+F \rightarrow CH_2CHCHFCH_2(\mathbf{2})$$
$$\rightarrow H + CH_2CHCFCH_2 \quad (2)$$
$$CH_2CHCHCH_2+F \rightarrow CH_2CHCHFCH_2(\mathbf{2})$$
$$\rightarrow C_2H_3+C_2H_3F \quad (3)$$
$$CH_2CHCHCH_2+F \rightarrow HF + CH_2CHCHCH \quad (4)$$
$$CH_2CHCHCH_2+F \rightarrow HF + CH_2CHCCH_2 \quad (5)$$

The relative energies and ZPEs of all reactants, products and transition states are compiled in Table I, while the vibrational frequencies are listed in Table II. The optimized geometries of intermediates and transition states for this reaction are shown in Fig.2. From the energy map shown in Fig.1, we have found four different reaction pathways that will lead to products from the F-atom reaction with *trans*-1,3-butadiene. Two of

TABLE II Vibration frequencies for reactants, products, intermediates, and transition states of the reaction of *trans* -1,3-butadiene with F atom at the B3LYP/6-311-g(d,p) level of theory.

Species	Frequencies/cm^{-1}	Species	Frequencies/cm^{-1}
HF	4095	$CH_2CHCHCH_2F$(**1**)	77,173,274,418,500,546,746,814,924,
C_2H_3	711,819,921,1046,1391,1651,3036,3134,3236		984,988,1004,1148,1207, 1244,
C_2H_3F	483,724,894,929,960,1154,1328,1407,1703,		1282,1334,1411,1496,1501,1521,
	3163,3204,3258		3013,3071,3121,3140,3150,3237
$CH_2CHCHCH$	162,291,486,582,720,826,898,934,939,1022,	$CH_2CHCHFCH_2$(**2**)	107,161,287,326,371,523,542,695,842,
	1154,1259,1319,1440,1619,1667,3086,3133		940,955,1020,1026,1117,1162,1294,
	3148,3222,3236		1313,1345,1444,1451,1691,3040,3128,
CH_2CHCCH_2	206,213,495,524,573,741,883,907,937,981,		3147,3149,3214,3263
	1090,1194,1376,1449, 1492,1909,3068,3111,	TS1	1204i, 125,201,258,448,473,499,536,
	3126,3151,3252		915,978,1043,1050,1134,1163,1198,
C_4H_6(*trans*-1,3	172,300,518,536,777,898,937,938,996,1002,		1271,1338,1474,1628,1787,3192,3203,
-butadiene)	1051,1226,1312, 1319, 1413,1473,1646,1699,		3252,3296
	3124,3133,3136,3137,3221,3221	TS2	1335i,145,268,382,465,505,555,612,
$CH_2CHCFCH_2$	160,267,435,447,590,723,759,822,897,947,		742,814,836,914,972,1061,1098,1158,
	951,1011,1049,1305,1327, 1419,1457,1663,		1319,1350,1430,1473,1630,2003,3210,
	1719,3152,3167,3191,3231,3242,		3229,3240,3308,3342
$CH_2CHCHCHF$	146,192,394,395,694,720,807,918,931,945,	TS3	644i, 78,185,211,297,396,500,652,811,
	1024,1036,1187,1259,1321,1382,1461,1655,		858,940,973,1020,1074,1125,1189,
	1714,3134,3159,3168,3219,3223		1327,1423,1435,1636,1919,3151,3226,
			3266,3274,3340

them are direct HF formation pathways that have no long-lived intermediates. In addition to the direct HF formation channels, two complex formation pathways were discovered in this study.

The first complex formation pathway is the relative stable radical $CH_2CHCHCH_2F$ (species **1**) pathway. This radical is formed via the F atom approaching the end carbon atom in the C_4H_6 molecule with the F atom attached to this carbon atom. In this process, the neighboring C=C double bond is downgraded to a single bond. The energy of the radical $CH_2CHCHCH_2F$ complex is lower by 201.5 kJ/mol than that of the reactants according to the calculations. Dynamically this complex can dissociate to form the $H+CH_2CHCHCHF$ channel via a transition state TS1, and the barrier is about 206.9 kJ/mol, slightly higher than the reactants. The energy for the product channel $H+CH_2CHCHCH_2F$ is found to be lower than that of the reactants by about 33.9 kJ/mol.

The second complex, $CH_2CHCHFCH_2$ (species **2**), is initially formed by the F atom approaching one of the two middle carbon atom of 1,3-butadiene. The radical complex $CH_2CHCHFCH_2$ lies lower than the reactants by about 153.4 kJ/mol in energy. From this complex formation pathway, the radical intermediate may undergo two dissociation channels: one by the F atom exchange with an H atom to form the $H+CH_2CHCFCH_2$ channel via TS2, the other by the dissociation of the middle C−C bond in the complex $CH_2CHCHFCH_2$ to form the $C_2H_3+C_2H_3F$ channel via the transition state

TS3, whose energy is higher than that of the transition state for the exchange reaction.

The heats of formation (at 298.15 K) for the reaction pathway (1) and (2) were determined to be 33.9 and 44.3 kJ/mol respectively in the present calculations. In the crossed beam study of the title reaction [15], the energetic limit of the product translational energy distribution for the H atom formation channel was shown to be about 79.4 kJ/mol at the collision energy of 23.8 kJ/mol, indicating that the maximum exothermicity of the H atom formation is about 54.3 kJ/mol. This is consistent with the current theoretical results. One of the interesting questions for the observed H atom formation channel is which pathway is preferred. From the energetic point of view, the two H atom formation pathways are all accessible. However, the dynamics of the two pathways are significantly different. Obviously, channel (1) occurs via the lowest complex formation pathway ($CH_2CHCHCH_2F$), while channel (2) occurs through an intermediate ($CH_2CHCHFCH_2$) that is about 48.1 kJ/mol higher than the lowest intermediate pathway. From the energetic point of view, channel (1) should be a more favorable intermediate pathway. The heat of formation for channel (2), however, is slightly larger than that for channel (1), while the reverse barrier for channel (1) is about 16.7 kJ/mol lower than that for channel (2). The transition state for channel (1) (TS1) is also slightly lower than that for channel (2) (TS2). However, the difference between the two channels in these properties is very significant,
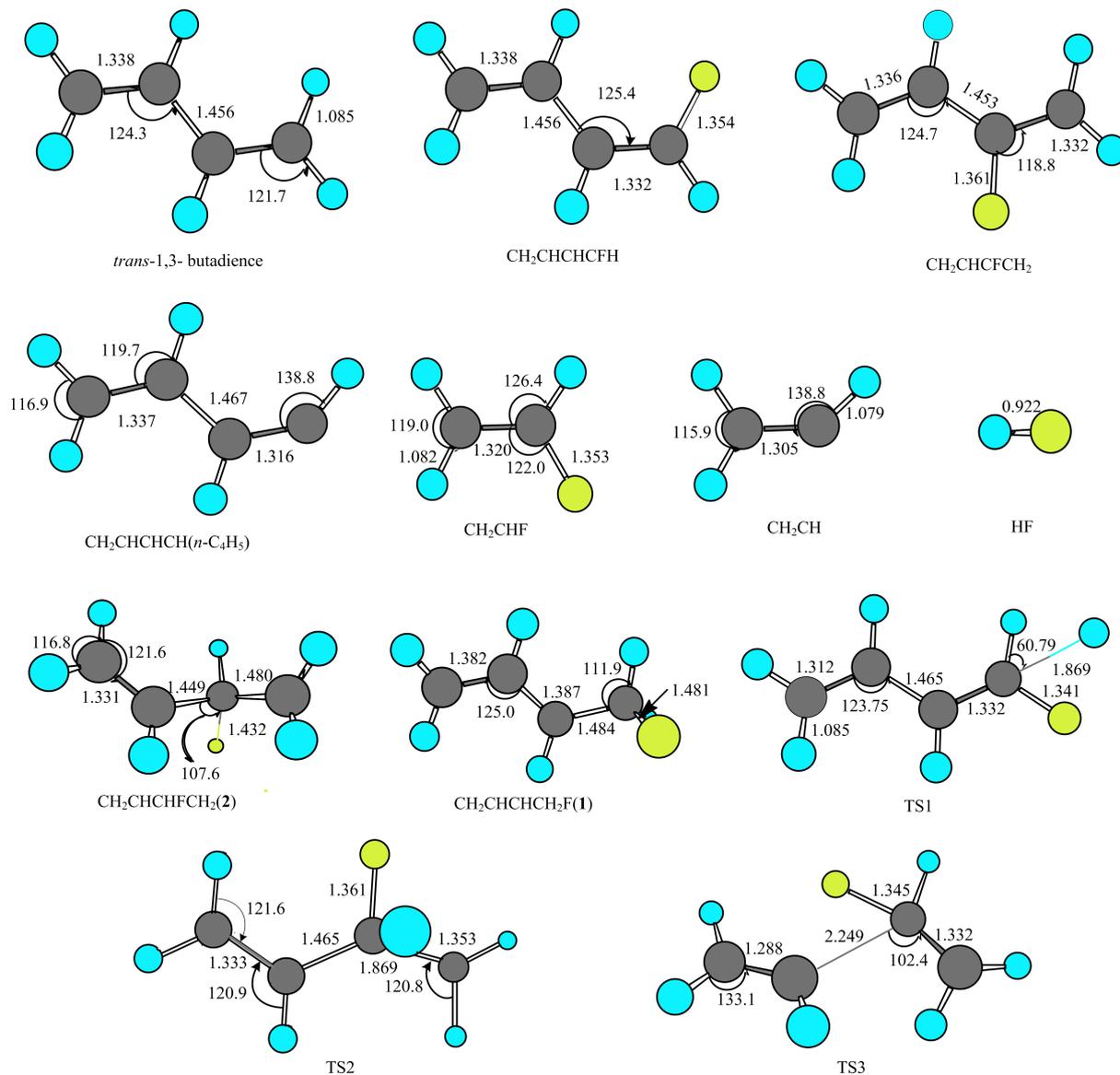
FIG. 2 The optimized geometries of reactants, intermediates, products, and transition states at the B3LYP/6-311G(d,p) level of theory for the reaction of F atom with *trans*-1,3-butadiene. The bond length and angle were in Å and (°) respectively.

therefore it is rather difficult to tell which pathway is more important for the H atom formation process observed in the crossed molecular beam experiment. From the above considerations, the relative importance of the two H atom formation pathways is likely determined by the complex formation step, rather than the dissociation step. Since energetically the formation of the $CH_2CHCHCH_2F$ complex is more favorable than that of the $CH_2CHCHFCH_2$ complex, it is quite likely that channel (1) is more important than channel (2) in the process. Furthermore, channel (2) is not the only reaction channel that occurs through the same intermediate, making the above argument more plausible.

In addition to the H atom formation channel, the $C_2H_3+C_2H_3F$ channel can also be formed via the

$CH_2CHCHFCH_2$ complex formation pathway through a different transition state, TS3. This channel is a simple C−C bond cleavage process from the intermediate. The calculated barrier is 178.1 kJ/mol, which is slightly larger than the value for the H product channel from the same intermediate. Since this channel is competing with the H atom formation pathway through the same intermediate, it is rather interesting to know the relative importance of these two channels from the same intermediate ($CH_2CHCHFCH_2$). In order to know the relative importance of these two channels, the RRKM method was used to calculate the rate constants for the two channel [20,21], and the calculated rate constant for the $C_2H_3+C_2H_3F$ product channel (3.57×10^6 s^{-1}) is smaller than that of the H product (4.28×10^6 s^{-1}),

so the relative branching ratio for these two channels via the same intermediate is 1:1.2. In the experimental study, this C−C bond breaking channel has not been observed. It is not surprising that this channel is probably minor relative to the total H atom formation channel according to the above analyses. Furthermore, the kinematics for this channel makes it much more (at least an order of magnitude) difficult to be observed in a crossed beam experiment since the reaction products (C_2H_3, C_2H_3F) will scattered into a much larger solid angle than the C_4H_5F product from the H atom channel.

For the direct reaction channel (4) and (5), the F atom approaches the C_4H_6 molecule, it will take away an H atom at the end carbon atoms or the middle carbon atoms to form the product HF. Since the F atom's eletronegativity is larger than the C atom, it will be rather easy to attract the H atom to form an HF molecule. For these two possible channels, two transition states, were found at the B3LYP/6-311G** level, but disappeared at the MP2/6-311G** level. The energies for these two transition states calculated at the CCSD(T) and B3LYP/6-311G(d,p) levels also show significant differences. Therefore, it is possible that the HF reaction channels proceed via abstraction mechanisms without well-defined transition states. From the energetic point of view, the HF channels are also less favorable than the two complex formation pathways, which is in agreement with the experimental observation that only the H atom formation channel is observed.

IV. CONCLUSION

In this paper, we have presented our theoretical studies of the $F+C_4H_6$ reaction at the CCSD(T)/6-311G(d,p)/B3LYP/6-311G(d,p) level. According to our calculations, the most favorable pathway for the title reaction is the F atom approaching in the direction perpendicular to the molecular plane of C_4H_6 to form the $CH_2CHCHCH_2F$ and $CH_2CHCHFCH_2$ complexes. The H atom is likely produced via these two complex formation pathways, in good agreement with previous experimental results in both energy and dynamics. For the C_2H_3 channel, the rate constant is a little smaller than that of the H atom formation process via the same intermediate **2** based upon RRKM calculations. Based on further theoretical analysis, we concluded that the $C_2H_3+C_2H_3F$ product channel should be noticeably less important than the H atom formation process. Theoretical calculations also show that the HF formation should occur via an abstraction mechanism. Further analysis also shows that the HF channel is likely to be a minor process due to the energetic considerations, suggesting that it is difficult to observe this channel in a crossed molecular experiment.

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