

ARTICLE

Direct Dynamics Simulation of Reaction Between F₂ and EthyleneYan qi^a, Ke-li Han^{a*}, António J. C. Varandas^b

a. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China; b. Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

(Dated: Received on August 28, 2005; Accepted on January 25, 2007)

Direct dynamics within the framework of DFT was used to study the long-time puzzling mechanism of the reaction between F₂ and ethylene. Three types of reactions are widely accepted: F atom elimination reaction, HF elimination reaction and the addition reaction. Several reaction mechanisms have been proposed, but only the radical mechanism can reasonably explain the initial reaction at low temperature. In this article, our calculations support the radical mechanism and the reaction mechanisms of the three reactions, and they are described in detail by trajectory simulation. The reactions in a cryogenic matrix with the reaction mechanism were also discussed.

Key words: Direct dynamics, Reaction mechanism, F₂ molecule, Ethylene

I. INTRODUCTION

A free radical mechanism has been postulated [1,2] for the reaction between F₂ and compounds with a C=C double bond in which the initiation step is F₂ dissociation, with the formed atoms acting as initiators of various free radical chain reactions. The dissociation requirement is very demanding since reaction could only occur after overcoming the energy barrier for bond breaking of F₂ of 160.1 kJ/mol [3]. Of course, its explosive nature at high temperatures could explain why enough thermal energy is available for the cleavage of the F-F bond. On the other hand, explosive chain reactions of free radicals may occur at low and moderate temperatures, even at -75°. In this case, it cannot explain the origin of the F radicals [2].

Hoping to eliminate the deficiency of the free radical mechanism for explaining the initiation of the reaction, together with investigations on reactions between fluorine and several halogen-substituted olefins, Miller *et al.* have proposed the following initiation step of the reaction [4,5]: $RC = CR' + F_2 \rightarrow R\cdot C - CR'\cdot F + \cdot F$. Such a mechanism has found support from other researchs. For example, it was found that olefin dimerization reactions [6,7] followed this radical initialization mechanism. On the other hand, unfavorable comments [8-11] also persist. For example, the reaction between F₂ and ethane in a cryogenic matrix illustrated characteristics drastically distinct [11] from those in vapor phase. The products have been identified to be vinyl fluoride and hydrogen fluoride in competition with 1,2-difluoroethane. The radical mechanism was ruled out, and a four-center addition mechanism derived [11] from experimental re-

sults.

There are also great discrepancies among theoretical calculations of the title reaction. Hartree-Fock calculations [12] using a 3-21G basis set gave rise to a four-centered transition structure for a concerted *syn* addition, with a barrier height of about 213.2 kJ/mol. An insertion mechanism was suggested by Iwoka *et al.* based on MP2/6-31G calculations [13]. Assuming the F₂ molecule was perpendicular to the C=C double bond, the system passed through a transition state structure in which one C-F bond was first formed, with a reaction barrier height of about 96.1 kJ/mol. A series of dynamics studies [14-16] of the reaction between F₂ and ethylene were performed both in gas phase and in low temperature matrices on a specially designed potential energy surface built on the assumption of a four-center concerted *syn* addition reaction and a barrier height artificially set at 51.4 kJ/mol. Moreover, the addition mechanism has also been studied by DFT theory using hybrid functionals [17]. These studies supported Miller's radical mechanism, and gave a diradical addition product with a low activation barrier of 7.5 and 26.3 kJ/mol, calculated at B3LYP/aug-cc-pvtz and BHH/aug-cc-pvtz levels, respectively. Such a barrier height lies close to the result of a kinetics study [18] that predicts the energy barrier for reaction between F₂ and ethylene to be 18.8 kJ/mol or so.

In this work we studied a direct dynamics simulation of the title reaction. To save computational time, the number of trajectories was drastically reduced, which is reflected by poor statistics of the calculated reaction rates and branching ratios. Since the major motivation was the elucidation of its mechanism, the results may still provide a deep insight into the reaction details. There are many successful examples of this technique [19-21].

* Author to whom correspondence should be addressed. E-mail: klhan@dicp.ac.cn

II. THEORETICAL APPROACH

Molecular dynamics simulations traditionally [22-24] require an experimental or an analytical potential energy surface built upon a full grid of *ab initio* points covering the relevant regions of the molecule configuration space [25]. Instead, in direct dynamics the classical trajectories are computed on the fly on an *ab initio* or DFT potential energy surface. Thus, the method will not be dependent on prior knowledge of the surface's topography or experimental assumptions about reaction pathways. With the advances in quantum chemistry and computational power, such an approach has become a general tool being specially suited for dynamics studies involving medium size polyatomics since reliable explicit global potential energy surfaces are then extremely hard to model. Of course, the computational cost prevents the use of expensive state-of-the-art *ab initio* correlated electronic structure calculations (thus accurate potential energy surfaces), but this may not be an overly strong limitation if only general trends are envisaged.

Both geometry optimization and trajectory simulations in our calculation were carried out within the DFT framework by using VASP [26-29] (Vienna *ab initio* Simulation Package) which has been successfully applied in other dynamic studies [19-21]. Specifically, a plane wave basis set with cutoff energy of 350 eV for dynamics simulation and 500 eV for geometry optimization was employed for the wave function. The generalized gradient approximation (GGA) [30,31] was used to describe the exchange-correlation function, and Vanderbilt ultrasoft pseudopotentials [32] were employed as supplied by VASP [33] to describe the atomic cores. A cubic supercell of side length 16 Å was assumed to model the reaction space, with each atom being allowed to relax completely holding the total energy constant (micro-canonical ensemble). For the integration over the Brillouin-zone, only the Γ point was used, which turned out to be sufficiently accurate.

As a limited number of trajectories were performed in dynamic simulation and attention was focused on the elucidation of reaction mechanism, we used a simple method for the initial geometry sample. Our trajectory simulations were initiated at the transition-state geometry obtained by DFT [17], and this structure was perturbed randomly by thermal excitation [19-21]. First, we carried out a preliminary simulation in vicinity of the transition state at a specified temperature 2000 K within a short duration. Then, we ran the trajectories by selecting the initial structures randomly from the configurations generated during the preliminary simulation. Initial velocities were randomly chosen according to a Boltzmann distribution defined by the simulation temperature 3500 K. The time step size was in all cases set at 0.5 fs and the trajectory was terminated at 1000 fs unless special instructions were given.

The accuracy of the approach can be assessed from

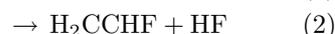
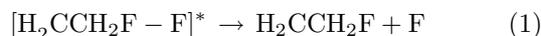
the calculated energetics. The reaction heats of the channels leading to $\text{CH}_2\text{CHF}+\text{F}$, $\text{CH}_2\text{CHF}+\text{HF}$, and gauche 1,2-fluoroethane products are -40.8 , -448.2 and -487.8 kJ/mol, respectively, which agree satisfactorily with the reported experimental values of -58.5 , -453.4 , and -485.3 kJ/mol [11], respectively. Furthermore, the diradical structure was obtained by geometry optimization, which further confirmed the reliability of our method. The structural parameters of the diradical $\text{H}_2\text{CCH}_2\text{F}-\text{F}$ and CH_2CHF , whose optimizations were carried out with spin polarity, are presented in Table I. They are close to the available data calculated at B3LYP/aug-cc-pvtz [17]. From reactants to the diradical, the overall energy change is -68.4 kJ/mol, in fair agreement with the best value of -76.9 kJ/mol obtained by using B3LYP [17] which has been overestimated since the binding energy of the van der Waals complex in the calculation is 2.5 kJ/mol higher than the value calculated by using MP2 theory.

TABLE I Structural parameters of the diradical structure and H_2CCHF , both calculated with VASP and with *ab initio* method at B3LYP/aug-cc-pvtz [17] level. Bond lengths and angles are in Å and degrees, respectively.

Parameter	Diradical		H_2CCHF	
	VASP	<i>ab initio</i>	VASP	<i>ab initio</i>
C-C	1.471	1.470	1.466	1.473
C-F	1.433	1.430	1.413	1.406
F-F	2.494	2.139		
C-H	1.094		1.107	1.098
$\angle\text{CCF}$	98.5	105.6	110.6	110.8

III. RESULTS AND DISCUSSION

In the 70 simulation trajectories, 23 led to dissociation toward the reactants (F_2 and ethylene); the remaining 47 trajectories were reactive. The results of our simulation trajectories firmly supported Miller's radical mechanism [4,5]. After formation of the C-F bond, the reactions can be divided into three categories :



In the reactive trajectories, 28 followed reaction (1), 17 followed reaction (2), 2 followed reaction (3) and one of the two led to homolysis of the C=C double bond.

A. F atom elimination reaction

The interatomic distances *vs.* reaction time plus snapshot of a sample trajectory that leads to reaction (1) are shown in Fig.1. The process is composed

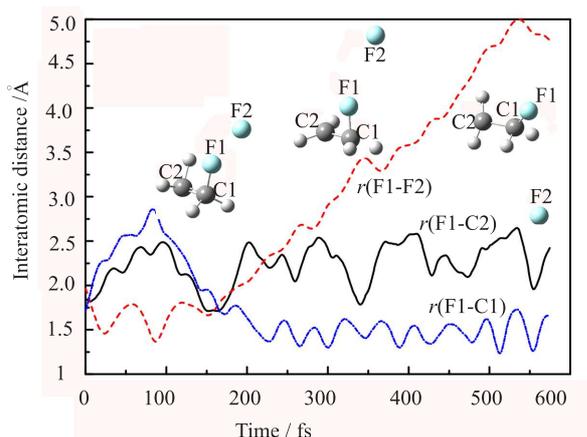


FIG. 1 Interatomic distances *vs.* reaction time plot plus snapshots of sample trajectories leading to reaction (1).

of two stages. The first stage is the C–F bond formation. Starting at equal distances with the two C atoms, F1 forms bond with C1 atom (at about 400 time steps). During the process, the distance between the two F atoms vibrates around the equilibrium value. The second stage begins with the C–F bond formation, while at the same time the F atom is left behind the H₂CCH₂F. This indicates that the diradical structure cleaved rapidly without any stabilization period.

B. HF elimination reaction

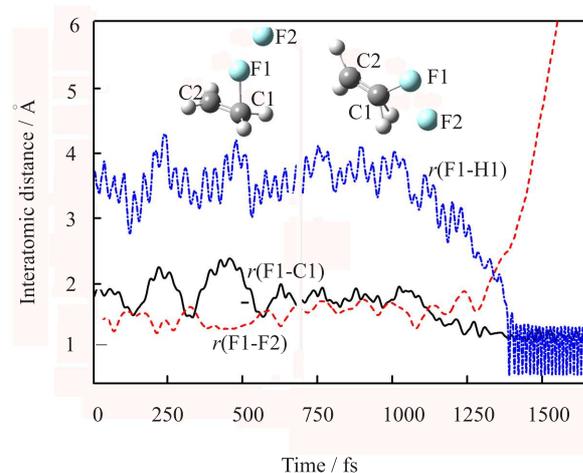


FIG. 2 Interatomic distances *vs.* reaction time plot plus snapshots of sample trajectories leading to reaction (2).

For reaction (2), we found two pathways. One of them performs the stepwise mechanism proposed by Wang *et al.* [17]. In the first step the F atom dissociates from the diradical, and in the second step the F atom attacks CH₂CH₂F and abstracts an H atom from the fluorinated methyl group. In our simulations, such

a stepwise reaction is found to occur with only a small probability. The other pathway, leading to HF elimination performing the concerted reaction mechanism, is predominant. The interatomic distances *vs.* reaction time plus snapshots of a sample trajectory leading to such a concerted process are shown in Fig.2. Obviously, it is the two hydrogen bonds which drag the tail F atom that leads to cleavage of the F–F bond.

C. Addition reaction

The addition products show the so-called “gauche effect” [34], about which rather sophisticated theoretical explanations have been posed [35]. The *syn* addition that presumably originates from the diradical cannot provide enough energy for the F atom to leave quickly, thus resulting in the formation of a second C–F bond. Furthermore, 1,2-difluoroethane has been found to be relatively stable by prolonging the reaction time to 3000 fs. The sample trajectory in Fig.3 shows the reaction process via a plot of interatomic distances *vs.* reaction time and snapshots. Clearly, the first C–F bond is formed after about 850 fs, at nearly the same time the F–F bond cleaves. Then, at about 1100 fs, the second C–F bond is formed.

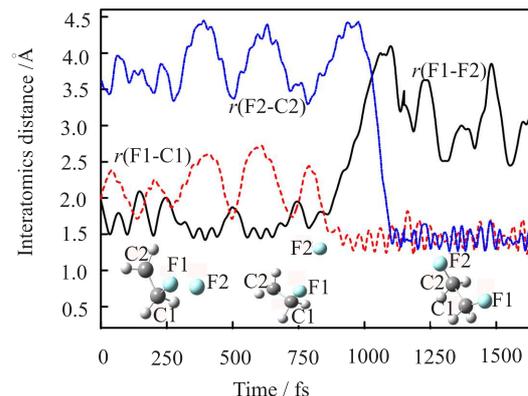


FIG. 3 Interatomic distances *vs.* reaction time plot plus snapshots of sample trajectories leading to reaction (3).

D. Reactions in cryogenic matrix

From experiments in cryogenic matrices, Frei *et al.* have ruled out the radical mechanism due to having not found CH₂CHF deposition and the gas fluorides, which were speculated as products of the reaction between F₂ and ethylene through the radical mechanism [11]. In fact, the reaction of *syn* addition and HF elimination can undoubtedly be prompted in the matrix under low temperature regimes. As the transitional energy of the F radical at least can partially transform into the environmental material, the F radical will be trapped

in the same host cage with the $\text{CH}_2\text{CH}_2\text{F}$ radical, and forced to bond with the nearby C atom or to abstract an H atom. Thus, it is impossible to build up considerable $\text{CH}_2\text{CH}_2\text{F}$ deposition, which can originate absorption bands strong enough to be observed. Furthermore, without enough transitional energy, the F radical will be unable to leave the cage to form gas fluorides.

From the discussion above, we may extract conclusions consistent with previous studies, in that the products of the reactions between F_2 and ethylene in a cryogenic matrix are 1,2-difluoroethen, vinyl fluoride, and HF. We also support the unanimously accepted conclusion that the HF elimination reaction occurs after the former 1,2-difluoroethen addition [11] noting that the exothermicity of 487.8 kJ/mol predicted for the addition reaction is large enough to overcome the energy barrier (259.2 kJ/mol) [36] of the HF elimination reaction. However, the concerted HF elimination may still play a key role and serve as initiator in a cryogenic matrix.

IV. CONCLUSION

A three-center mechanism is suggested for the reaction between F_2 and ethylene. The short-lived diradical was found to follow three types of reaction (F atom elimination reaction, HF atom elimination reaction and addition reaction). Detailed mechanisms for each reaction are described. Most of the HF elimination reactions proceeded by the concerted mechanism, and the addition reaction proceeded by the stepwise mechanism. We also explain the experimental results in cryogenic matrices within the mechanism.

V. ACKNOWLEDGMENTS

This work was supported by the National Key Basic Research Special Funds (No. 1999075302), the Knowledge Innovation Program of the Chinese Academy of Sciences (INF105-SCE-02-08) and the National Natural Science Foundation of China (No.20373071, No.20333050). The support from Fundação para a Ciência e Tecnologia, Portugal, is also gratefully acknowledged.

- [1] W. T. Miller Jr., *J. Am. Chem. Soc.* **62**, 341 (1940).
- [2] L. A. Bigelow, *Chem. Revs.* **40**, 51 (1947).
- [3] E. A. Colbourn, M. Dagenais, A. E. Douglas and J. W. Raymonda, *Can. J. Phys.* **54**, 343 (1976).
- [4] W. T. Miller Jr. and A. L. Dittman, *J. Am. Chem. Soc.* **78**, 2793 (1956).
- [5] W. T. Miller Jr., S. D. Koch Jr. and F. W. McLafferty, *J. Am. Chem. Soc.* **78**, 4992 (1956).

- [6] W. T. Miller Jr. and S. D. Koch Jr., *J. Am. Chem. Soc.* **79**, **18**, 3084 (1956).
- [7] W. T. Miller Jr, J. O. Staffer, J. Fuller, G. Fuller and A. C. Currie, *J. Am. Chem. Soc.* **51**, 86 (1964).
- [8] S. Rozen and M. Brand, *J. Org. Chem.* **51**, 3607 (1986).
- [9] M. F. Ruasse, *Acc. Chem. Res.* **23**, 87 (1990).
- [10] Y. Kurosaki, *J. Mol. Struct. Theorchem.* **503**, 231 (2000).
- [11] H. Frei, L. Fredin and G. C. Pimentel, *J. Chem. Phys.* **74**, 397 (1981).
- [12] S. Yamabe, T. Minato and S. Inagaki, *J. Chem. Soc. Chem. Commun.* **532**, (1988).
- [13] T. Iwaoka, C. Kaneko, A. Shigihara and H. Ichikawa, *J. Phys. Org. Chem.* **6**, 195 (1993).
- [14] L. M. Raff, *J. Phys. Chem.* **91**, 3266 (1987).
- [15] M. J. Raff, *J. Chem. Phys.* **95**, 8901 (1991).
- [16] M. J. Raff, *J. Chem. Phys.* **93**, 3160 (1990).
- [17] B. W. Wang, L. Chan, S. P. Chan, Z. D. Chen and Z. F. Liu, *J. Chem. Phys.* **120**, 9476 (2004).
- [18] G. A. Kapralora, A. M. Chaikin and A. E. Shilov, *Kinet. Katal.* **8**, 421 (1967).
- [19] Z. F. Liu, C. K. Siu and J. S. Tse, *Chem. Phys. Lett.* **314**, 317 (1999).
- [20] W. L. Yim and Z. F. Liu, *J. Am. Chem. Soc.* **123**, 2243 (2002).
- [21] W. C. Hon, Z. D. Chen and Z. F. Liu, *J. Phys. Chem. A* **106**, 6792 (2002).
- [22] T. K. Gu, Y. H. Qi and J. Y. Qin, *Chin. J. Chem. Phys.* **16**, 385 (2003).
- [23] H. R. Cong, X. F. Bian, H. Li and L. Wang, *Chin. J. Chem. Phys.* **15**, 288 (2002).
- [24] L. Zhang, Z. K. Zhong, Z. Y. Zhu, Y. Sun and Z. H. Zhu, *Chin. J. Chem. Phys.* **16**, 455 (2003).
- [25] A. J. C. Varandas, *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, D. Yarkony, H. Koppel and W. Domcke (Eds.). *Advanced Series in Physical Chemistry*. Vol. 15, Ch. 5. Singapore: World Scientific Publishing, (2004).
- [26] G. Kresse and J. Furthmüller, *J. Phys. Rev. B* **54**, 11169 (1996).
- [27] G. Kresse and J. Hafner, *Phys. Rev. B* **47**, RC558 (1993).
- [28] G. Kresse, *Technische Universität Wien*, (1993).
- [29] G. Kresse and J. Furthmüller, *J. Comput. Matter. Sci.* **6**, 15 (1996).
- [30] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- [31] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B* **48**, 4978 (1993).
- [32] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- [33] G. Kresse and J. Hafner, *J. Phys.: Condens. Matter.* **6**, 8245 (1994).
- [34] S. Wolfe, *Acc. Chem. Res.* **5**, 102 (1972).
- [35] D. Friesen and K. Hedberg, *J. Am. Chem. Soc.* **102**, 3987 (1980).
- [36] S. W. Benson and G. Haugen, *J. Phys. Chem.* **69**, 3898 (1965).