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# Coupled Cluster and Second-Order Møller−Plesset Perturbation Studies of the Mechanism of the Gas-Phase Atom−Radical Reaction of Atomic Hydrogen with $CF_2$ Radical

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The mechanism for the reaction of $CF_2$ radicals with H atoms has been examined using coupled cluster theory. There are two competing pathways for the formation of the products CF + HF. The first pathway involves direct abstraction of fluorine from $CF_2$ by H atoms, the barrier for which is 46.5 kcal mol$^{-1}$. The second pathway involves the addition of H atoms to $CF_2$ to form $CF_2H$, followed by a three-center elimination of HF. The overall barrier for these two steps is 10.0 kcal mol$^{-1}$.

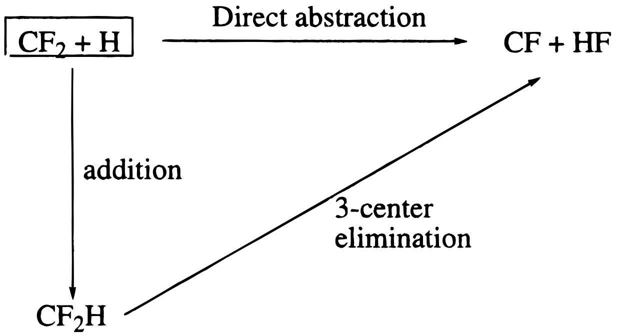
## I. Introduction

One of the most efficient materials used to extinguish unwanted fires has been Halon 1301 ($CF_3Br$). An unfortunate side effect of this compound is that its release into the atmosphere introduces bromine into the atmosphere. Atmospheric bromine is quite effective in removing ozone, particularly in the stratosphere. As a consequence, there have been protocols adopted to halt the production of Halons such as Halon 1301. Because there is a need to find replacements for these efficient fire extinguishing agents, most efforts have been directed at perfluorocarbon and hydrofluorocarbon materials as alternatives. The mechanism by which these materials act to extinguish flames is not well understood. Some studies have suggested that the $CF_3$ group of Halon 1301 ($CF_3Br$) in the alternative materials contributes $CF_3$ radicals that act to play a role in the combustion mechanism.[1−7] There have been a growing number of experimental studies directed at interrogating flames seeded with fluorinated materials to identify species that may be playing an important role in the flame inhibition chemistry. In early studies aimed at characterizing the flame chemistry involving $CF_3Br$, Biordi identified the $CF_2$ radical as a critical species involved in the inhibition chemistry.[1] Recent laser-induced fluorescence studies of perfluorinated and hydrofluorinated materials have also identified $CF_2$ directly in flames.[8−10] The key flame propagating species are H atoms, OH, and $HO_2$ radicals. It has been suggested that the main consumption route for $CF_2$ radicals is by their reaction with hydrogen atoms, viz.

$$CF_2 + H \rightarrow CF + HF \tag{1}$$

The $CF_2$ + H reaction is also considered to be one of the key reactions responsible for the production of HF. This reaction, although simple, is not well understood in terms of its kinetics or mechanism. Biordi[3] suggested that the rate coefficient is 3 × $10^{13}$ cm$^3$ mol$^{-1}$ s$^{-1}$ (5.0 × $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) at 1800 K. Ryan and Plumb[11] measured the room temperature rate coefficient for the $CF_2$ + H reaction to be 1.6 ± 0.4 × $10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Tsai and McFadden,[12] in a later study, measured the room temperature rate coefficient to be 3.9 ± 0.7 × $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The rate reported by Tsai and McFadden[12] is almost 250 times faster than that of Ryan and Plumb.[11] The product analysis studies of Tsai and McFadden[12] implied that the $CF_2$ + H reaction proceeded by fluorine atom abstraction. However, the question of whether it proceeded by direct abstraction of fluorine from $CF_2$ or by addition of hydrogen atoms to $CF_2$ to form a stable intermediate complex followed by a 1,1-HF elimination could not be addressed by the studies of Tsai and McFadden.[12]

**SCHEME 1. Reaction Scheme for the $CF_2$ + H Reaction**



The $CF_2$ + H reaction is a key reaction in models used to understand how new fluorinated substitutes inhibit flames; yet, mechanistic details of this reaction are not well understood. In the present study, ab initio molecular orbital theory is used to explore the mechanism of the $CF_2$ + H reaction. Specifically, the question of whether direct fluorine abstraction versus addition is the preferred pathway is explored by the mechanistic scheme shown in Scheme 1.

## II. Computational Methods

Geometries for reactants, products, intermediate complexes, and transition states are optimized using unrestricted second-order Møller−Plesset perturbation theory (UMP2)[13,14] and the unrestricted coupled cluster singles and doubles approach, including the effect of connected triples, determined using perturbation theory (UCCSD(T)).[15−17] In the coupled cluster calculations, the geometry from the UMP2 calculation along with its Hessian is used in the optimization for the minimum energy structure and for the location of the transition state. In the UMP2 optimization, the analytical gradient method developed by Schlegel[18] is used, while in the UCCSD(T) optimiza-

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**TABLE 1: Geometries of Species (Å and degrees) Involved in the Isodesmic Reaction**

| | | MP2 | | | CCSD(T) | | |
|---|---|---|---|---|---|---|---|
| species | coordinate | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) | 6-31G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) |
| CH | r(CH) | 1.119 | 1.111 | 1.111 | 1.129 | 1.121 | 1.121 |
| CF | r(CF) | 1.272 | 1.273 | 1.267 | 1.281 | 1.281 | 1.274 |
| $CH_2$ | r(CH) | 1.110 | 1.102 | 1.102 | 1.117 | 1.110 | 1.109 |
| | $\theta$(HCH) | 101.4 | 101.6 | 101.8 | 101.0 | 101.2 | 101.6 |
| $CF_2$ | r(CF) | 1.299 | 1.300 | 1.293 | 1.305 | 1.306 | 1.299 |
| | $\theta$(FCF) | 105.1 | 104.9 | 105.1 | 104.8 | 104.7 | 105.0 |
| $CH_3$ | r(CH) | 1.079 | 1.071 | 1.072 | 1.084 | 1.079 | 1.078 |
| $CH_2F$ | r(CH) | 1.081 | 1.074 | 1.074 | 1.086 | 1.079 | 1.079 |
| | r(CF) | 1.339 | 1.340 | 1.336 | 1.343 | 1.343 | 1.335 |
| | $\theta$(HCF) | 114.4 | 114.5 | 114.9 | 114.5 | 114.6 | 115.0 |
| $CF_2H$ | r(CH) | 1.087 | 1.080 | 1.082 | 1.091 | 1.085 | 1.086 |
| | r(CF) | 1.326 | 1.327 | 1.320 | 1.330 | 1.330 | 1.323 |
| | $\theta$(HCF) | 113.7 | 113.8 | 114.1 | 113.7 | 113.8 | 114.1 |

**TABLE 2: Total (hartree) and Zero-Point Energies (kcal mol$^{-1}$) for Species Involved in the Isodesmic Reaction**

| | MP2 | | | CCSD(T) | | | | |
|---|---|---|---|---|---|---|---|---|
| species | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) | 6-311++G(3df,3p) | ZPE |
| CH | −38.37996 | −38.38885 | −38.39645 | −38.38961 | −38.39829 | −38.40572 | −38.41030 | 4.2 |
| CF | −137.53653 | −137.57005 | −137.60418 | −137.52477 | −137.55572 | −137.59126 | −137.60351 | 1.9 |
| $CH_2$ | −39.02238 | −39.03465 | −39.04404 | −39.03473 | −39.04599 | −39.05546 | −39.06196 | 10.7 |
| $CF_2$ | −237.30432 | −237.36573 | −237.42748 | −237.27468 | −237.73071 | −237.39555 | −237.41848 | 4.5 |
| $CH_3$ | −39.72567 | −39.73907 | −39.74929 | −39.73225 | −39.74402 | −39.75458 | −39.76131 | 18.9 |
| $CH_2F$ | −138.81027 | −138.84872 | −138.88452 | −138.79890 | −138.83361 | −138.87137 | −138.88846 | 16.0 |
| $CF_2H$ | −237.91153 | −237.97481 | −238.03646 | −237.88059 | −237.93816 | −238.00336 | −238.02915 | 12.4 |

tion, the eigenvalue following algorithm is used. Initial searches used the 6-311G(d,p) basis set to optimize all of the structures. This basis set is expanded by the addition of d-polarization functions and f-polarization functions. The final geometries are computed using the 6-311G(2df,2p) basis set. The zero-point energy is computed as one-half the sum of the UMP2/6-311G(d,p) harmonic frequencies, which are not scaled. To improve the energy results, the basis set is further expanded to include diffuse functions, i.e., the 6-311++G(3df,3pd) basis set. All calculations are performed using the *Gaussian 94* suite of programs.[19]

## III. Results and Discussion

**A. Thermochemistry of the $CF_2H$ Intermediate.** The $CF_2H$ intermediate results from the addition of hydrogen atoms to $CF_2$ radicals. McMillen and Golden[20] estimate the heat of formation of the $CF_2H$ radical at 0 K to be −59.2 ± 5 kcal mol$^{-1}$. Pickard and Rodgers[21] have experimentally derived the heat of formation value at 298 K for $CF_2H$ as −57.1 ± 1 kcal mol$^{-1}$. To evaluate the heat of formation for $CF_2H$, two isodesmic reaction schemes are used. An isodesmic reaction is one in which the number of each type of bond and the spin multiplicities are conserved in the reaction scheme. The two isodesmic schemes are as follows:

$$CF_2H + CH_2 \rightarrow CH_3 + CF_2 \tag{2}$$

$$CF_2H + CH \rightarrow CH_2F + CF \tag{3}$$

The species involved in these isodesmic reactions have been fully optimized at the various levels of theory. Table 1 contains the optimized geometries for all of the species. The total and zero-point energies that have been determined from vibrational frequency calculations at the MP2/6-311G(d,p) level of theory are included in Table 2. Likewise, values for the heats of formation for CH, CF, $CH_2$, CHF, and $CF_2$ that are used in the isodesmic reaction are provided in Table 3. The literature value for $CH_2$ is taken from the most recent study of Litorja and Ruscic[22] for the ground state of $CH_2$. Since the ground state of $CH_2$ is a triplet state, to conserve spin in the isodesmic schemes, we have to use the heat of formation for $CH_2$ in the singlet state. The singlet−triplet splitting correction[23−25] has to be added. Using the singlet−triplet splitting in $CH_2$ at 3156 ± 5 cm$^{-1}$, along with the Litorja and Ruscic[22] measurement of the heat of formation of $CH_2$, leads to a heat of formation of the singlet state of 102.2 ± 0.3 kcal mol$^{-1}$.

**TABLE 3: Known Thermodynamic[a] Constants (kcal mol$^{-1}$) for Species Involved in the Isodesmic Reaction**

| species | $\Delta H_{f,0}{}^0$ |
|---|---|
| H | 51.634 ± 0.001 |
| HF | −65.129 ± 0.4 |
| CH | 141.18 ± 4 |
| CF | 60.1 ± 2 |
| $CH_2$ | 93.2 ± 0.3 |
| $CF_2$ | −43.6 ± 1.5 |
| $CH_2F$ | −4.5 ± 3 |
| $CH_3$ | 36.619 ± 0.2 |

[a] Values taken from Chase, M. S.; Davies, C. A.; Downey, J. R.; Frarip, D. J.; McDonald, R. A.; Syverad, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1).

Results of the heat of formation for the two isodesmic reactions are given in Table 4. It is interesting to note that within a given method, there is not a large variation among values. The difference between the MP2 and CCSD(T) results is, on average, about 2 kcal mol$^{-1}$ for the isodesmic scheme. At the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory, the difference for the two isodesmic schemes is only 0.1 kcal mol$^{-1}$. Within an isodesmic scheme, there appears to be reasonable cancellation of errors. Taking the average of the two isodesmic schemes, the heat of formation of $CF_2H$ is estimated as −53.8 ± 3 kcal mol$^{-1}$. Given the uncertainties in this result, it is within the error limits of the McMillen and Golden[18] experimentally derived value.

**B. Mechanism for the $CF_2$ + H Reaction.** Optimized geometries for the reactants, products, and transition states are presented in Table 5. The corresponding vibrational frequencies are given in Table 6. Total and relative energies for all species

**TABLE 4: Heats of Formation and Reaction (kcal mol$^{-1}$) for the $CF_2H$ Reaction from Isodesmic Scheme**

| isodesmic scheme | method | basis set | $\Delta H_{r,0}^0$ | $\Delta H_{f,0}^0$ ($CF_2H$) |
|---|---|---|---|---|
| $CF_2H + CH_2 \rightarrow CH_3 + CF_2$ | MP2 | 6-311G(d,p) | −60.0 | −49.2 |
| | | 6-311G(2d,2p) | −59.5 | −49.7 |
| | | 6-311G(2df,2p) | −60.1 | −49.1 |
| | CCSD(T) | 6-311G(d,p) | −57.2 | −52.0 |
| | | 6-311G(2d,2p) | −56.5 | −52.6 |
| | | 6-311G(2df,2p) | −57.0 | −52.0 |
| | | 6-311++G(3df,3pd) | −55.3 | −53.8 |
| $CF_2H + CH \rightarrow CH_2F + CF$ | MP2 | 6-311G(d,p) | −33.4 | −52.2 |
| | | 6-311G(2d,2p) | −33.3 | −52.3 |
| | | 6-311G(2df,2p) | −33.7 | −51.9 |
| | CCSD(T) | 6-311G(d,p) | −32.2 | −53.3 |
| | | 6-311G(2d,2p) | −31.9 | −53.7 |
| | | 6-311G(2df,2p) | −32.3 | −53.3 |
| | | 6-311++G(3df,3pd) | −31.7 | −53.9 |

**TABLE 5: Geometries (Å and degrees) for Reactants, Intermediates, Products, and Transition States for the $CF_2 + H$ Reaction**

| | | MP2 | | | CCSD(T) | | |
|---|---|---|---|---|---|---|---|
| species | coordinate | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) |
| | | | Reactants and Products | | | | |
| CF | $r$(CF) | 1.272 | 1.273 | 1.267 | 1.281 | 1.281 | 1.274 |
| HF | $r$(HF) | 0.912 | 0.914 | 0.914 | 0.913 | 0.914 | 0.914 |
| $CF_2$ | $r$(CF) | 1.299 | 1.300 | 1.293 | 1.305 | 1.306 | 1.299 |
| | $\theta$(FCF) | 105.1 | 104.9 | 105.1 | 104.8 | 104.7 | 105.0 |
| $CF_2H$ | $r$(CF) | 1.326 | 1.327 | 1.320 | 1.330 | 1.330 | 1.323 |
| | $r$(CH) | 1.087 | 1.080 | 1.082 | 1.091 | 1.085 | 1.086 |
| | $\theta$(FCH | 113.7 | 113.8 | 114.1 | 113.7 | 113.8 | 114.1 |
| | | | Transition State | | | | |
| $CF_2 + H \rightarrow CF + HF$ | $r$(HF′) | 1.188 | 1.189 | 1.177 | 1.258 | 1.263 | 1.320 |
| | $r$(CF)′ | 1.674 | 1.675 | 1.670 | 1.713 | 1.715 | 1.771 |
| | $r$(CF) | 1.252 | 1.252 | 1.247 | 1.264 | 1.263 | 1.250 |
| | $\theta$(HF′C) | 175.6 | 175.8 | 175.9 | 174.3 | 174.1 | 175.3 |
| | $\theta$(F′CF) | 100.1 | 100.2 | 100.1 | 100.1 | 100.2 | 98.8 |
| | $\tau$(HF′CF) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $CF_2 + H \rightarrow CF_2H$ | $r$(CH) | 2.275 | 2.306 | 2.300 | 2.357 | 2.422 | 2.427 |
| | $r$(CF) | 1.297 | 1.296 | 1.298 | 1.305 | 1.305 | 1.299 |
| | $\theta$(FCH) | 105.5 | 103.5 | 103.5 | 106.1 | 103.8 | 103.7 |
| | $\tau$(FCHF) | 111.0 | 108.0 | 108.1 | 111.3 | 109.4 | 109.6 |
| $CF_2H \rightarrow CF + HF$ | $r$(HF′) | 1.179 | 1.184 | 1.169 | 1.218 | 1.222 | 1.204 |
| | $r$(CF) | 1.270 | 1.269 | 1.264 | 1.279 | 1.278 | 1.272 |
| | $r$(CF′) | 1.800 | 1.813 | 1.798 | 1.827 | 1.836 | 1.819 |
| | $r$(CH) | 1.235 | 1.237 | 1.243 | 1.227 | 1.229 | 1.236 |
| | $\theta$(F′CH) | 40.6 | 40.4 | 40.2 | 41.4 | 41.3 | 41.1 |
| | $\theta$(F′CF) | 105.8 | 105.8 | 105.4 | 103.8 | 104.0 | 103.7 |
| | $\tau$(FCF′H) | 124.0 | 124.3 | 125.0 | 119.1 | 119.5 | 120.2 |

**TABLE 6: Vibrational Frequencies (cm$^{-1}$) for Species Involved in the $CF_2 + H$ Reaction**

| species | frequencies (cm$^{-1}$) |
|---|---|
| | Reactants and Products |
| HF | 4254 |
| CF | 1348 |
| $CF_2$ | 1283, 1175, 685 |
| $CF_2H$ | 3210, 1398, 1229, 1203, 1076, 558 |
| | Transition States |
| $CF_2 + H \rightarrow CF + HF$ | 1405, 1121, 1091, 530, 361, 3097i |
| $CF_2 + H \rightarrow CF_2H$ | 1280, 1174, 690, 224, 178, 569i |
| $CF_2H \rightarrow CF + HF$ | 2338, 1378, 966, 782, 309, 1808i |

involved in the $CF_2 + H$ reaction are listed in Tables 7 and 8, respectively.

*1. Direct Abstraction of Fluorine by H Atoms.* In the transition state for the direct abstraction of fluorine by H atoms, the hydrogen approaches the fluorine almost collinearly. The HF′C angle at the CCSD(T)/6-311G(2df,2p) level of theory is 175.3°, as shown in Figure 1a. The HF′ bond is nearly 71% formed at the MP2/6-311G(2df,2p) level of theory, while at the CCSD(T)/6-311G(2df,2p) level of theory the HF′ bond is nearly 56% formed relative to the HF bond in the isolated HF. At the MP2 level, the HF′ bond is generally predicted to be more nearly formed than at the CCSD(T) level. A similar trend is also seen in the breaking of the CF′ bond. At the MP2 level, the CF′ bond is shorter than that predicted at the CCSD(T) level. The differences in the CF′ bond length range from 0.039 to 0.101 Å between the MP2 and CCSD(T) levels of theory. These changes suggest that the MP2 level of theory predicts a transition structure that is later in the entrance channel than at the CCSD(T) level. The transition state structure for the $CF_2 + H$ direct fluorine abstraction reaction has been verified to be a first-order saddle point. The vibrational frequency for the transition state stretch is characterized by one imaginary frequency at 3097i cm$^{-1}$. The transition state vectors for this imaginary frequency indicate that the main motion is characterized by the forming HF′ bond, coupled with the breaking CF′ bond motions. This is consistent with the geometrical changes shown in Table 5.

The heat of reaction for the direct abstraction is best estimated to be −13.2 kcal mol$^{-1}$ at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory. From the experimental heats of formation for the reactants and products of the reaction given in Table 3, the experimental heat of reaction is estimated as −13.1 ± 2 kcal mol$^{-1}$. There is a 0.1 kcal mol$^{-1}$ difference between the highest CCSD(T) level of theory with experiment. Note that, at the MP2 level of theory, the heat of reaction is

**TABLE 7: Total Energies (hartrees) for Reactants, Intermediates, Products, and Transition States for the $CF_2 + H$ Reaction**

| | MP2 | | | CCSD(T) | | | CCSD(T) |
|---|---|---|---|---|---|---|---|
| species | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) | 6-311G(d,p) | 6-311G(2d,2p) | 6-311G(2df,2p) | 6-311++G(3df,3pd) |
| Reactants and Products | | | | | | | |
| H | −0.49981 | −0.49981 | −0.49981 | −0.49981 | −0.49981 | −0.49981 | −0.49981 |
| HF | −100.28608 | −100.31420 | −100.33600 | −100.27379 | −100.29995 | −100.32353 | −100.34139 |
| CF | −137.53653 | −137.57005 | −137.60418 | −137.52477 | −137.55572 | −137.59126 | −137.60351 |
| $CF_2$ | −237.30432 | −237.36573 | −237.42748 | −237.27468 | −237.33071 | −237.39555 | −237.41848 |
| $CF_2H$ | −237.91153 | −237.97481 | −238.03646 | −237.88059 | −237.93816 | −238.00336 | −238.02915 |
| Transition States | | | | | | | |
| $CF_2 + H \rightarrow CF + HF$ | −237.71194 | −237.77511 | −237.84480 | −237.69769 | −237.75586 | −237.81713 | −237.84721 |
| $CF_2 + H \rightarrow CF_2H$ | −227.79659 | −237.85858 | −237.92025 | −237.77262 | −237.82961 | −237.89448 | −237.91760 |
| $CF_2H \rightarrow CF + HF$ | −237.78422 | −237.84799 | −237.90652 | −237.75921 | −237.81750 | −237.87921 | −237.90817 |

**TABLE 8: Heats of Reaction[a] and Barrier Heights[a] for the $CF_2 + H$ Reaction**

| | $CF_2 + H \rightarrow CF_2H$ | | $CF_2H \rightarrow CF + HF$ | | $CF_2 + H \rightarrow CF + HF$ | |
|---|---|---|---|---|---|---|
| level of theory | $\Delta H_{r,0}^0$ | barrier | $\Delta H_{r,0}^0$ | barrier | $\Delta H_{r,0}^0$ | barrier |
| MP2/6-311G(d,p) | −59.5 | 5.3 | 51.4 | 75.7 | −8.1 | 59.7 |
| MP2/6-311G(2d,2p) | −60.7 | 5.0 | 52.4 | 75.4 | −8.2 | 58.6 |
| MP2/6-311G(2df,2p) | −60.6 | 5.0 | 56.0 | 77.3 | −4.6 | 53.7 |
| CCSD(T)/6-311G(d,p) | −58.7 | 1.8 | 47.1 | 72.0 | −11.6 | 48.8 |
| CCSD(T)/6-311G(2d,2p) | −59.6 | 1.2 | 47.4 | 71.5 | −12.2 | 48.7 |
| CCSD(T)/6-311G(2df,2p) | −59.9 | 1.2 | 51.2 | 73.7 | −8.7 | 51.0 |
| CCSD(T)/6-311++G(3df,3pd)[b] | −61.7 | 1.0 | 48.5 | 71.7 | −13.2 | 46.5 |
| exptl | | | | | −13.1 ± 2 | |

[a] In units of kcal $mol^{-1}$. [b] Calculated with geometries calculated at the CCSD(T)/6-311G(2df,2p) level of theory.

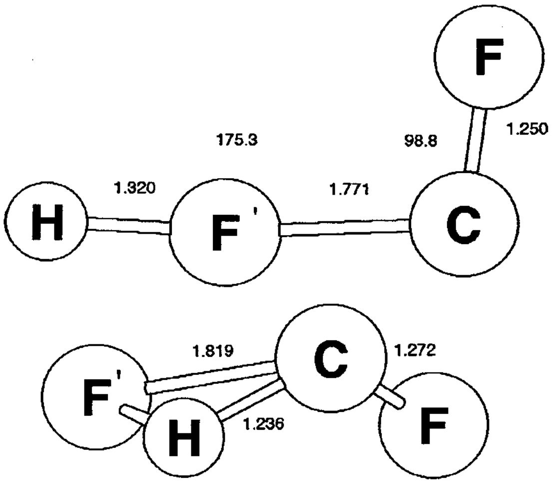

**Figure 1.** Transition states for the $CF_2 + H$ reaction. The values are taken from Table 5 from the CCSD(T)/6-311G(2df,2p) level of theory. (a) Direct abstraction pathway. (b) 3-Center elimination pathway.

generally underestimated by 3−4 kcal $mol^{-1}$ compared to the CCSD(T) levels. The barrier for the direct abstraction reaction is also generally overestimated at the MP2 level compared to the CCSD(T) level of theory. The best estimated barrier is 46.5 kcal $mol^{-1}$ for the direct abstraction reaction, as calculated at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level. The large barrier for the direct abstraction reaction is not unreasonable, since direct attacks on fluorine in closed-shell systems generally tend to have high barriers associated with them. More recent work[26] on the CHF + H reaction has shown that the direct abstraction of fluorine from CHF by H atoms is also similarly high, i.e., 37.8 kcal $mol^{-1}$.

In relation to the experimental studies of Ryan and Plumb[11] and those of Tsai and McFadden,[12] with a barrier of 46.5 kcal $mol^{-1}$ for the direct fluorine abstraction pathway, it is very unlikely that the rate and observed products result from this route. This suggests that the probable reaction mechanism for the $CF_2 + H$ reaction first must involve addition of hydrogen atom to form a stable $CF_2H$ intermediate complex followed by 1,1-HF elimination from the $CF_2H$ radical.

*2. Addition of H Atoms Pathway and the $CF_2H$ Intermediate.* In the addition of hydrogen atom to $CF_2$, the transition state for the reaction appears to be located in the long-range part of the potential. This is indicated by the long CH bond that ranges from 2.27 to 2.36 Å. It is interesting to note that the MP2 level of theory predicted the transition state to be further into the entrance channel than the CCSD(T) level of theory. Both MP2 and CCSD(T) levels of theory predict that the transition state resembles more of the reactant character. For example, at the MP2/6-311G(2df,2p) level of theory, the CF bond length in $CF_2$ is 1.293 Å, while the CF bond length in the $CF_2 + H$ addition transition state is 1.291 Å. Similar trends are observed for the other levels of theory. The vibrational frequency analysis shows that the transition state has one imaginary frequency of magnitude 569i $cm^{-1}$. The transition state vectors show that the dominant motion is characterized by the carbon−hydrogen stretching motion.

The addition of a hydrogen atom to $CF_2$ yields the $CF_2H$ radical. The heat of reaction for this process is −61.7 kcal $mol^{-1}$, as predicted at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory. McMillen and Golden[20] estimate the heat of formation of $CF_2H$ radical at 0 K to be −59.2 ± 5 kcal $mol^{-1}$. Using the heat of formation values for $CF_2$ and H atoms given in Table 3, we estimate the heat of reaction for the $CF_2 + H \rightarrow CF_2H$ reaction to be −67.2 ± 5 kcal $mol^{-1}$. This result deviates by 5.5 kcal $mol^{-1}$ from the result calculated at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory. If we use the derived heat of formation value for $CF_2H$ (−53.8 ± 3 kcal $mol^{-1}$) from the isodesmic reaction scheme, we estimate the heat of reaction for the $CF_2 + H \rightarrow CF_2H$ channel to be −61.8 kcal $mol^{-1}$. This value differs from the direct CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) determination by 0.1 kcal $mol^{-1}$. This suggests that the isodesmic heat of formation value for $CF_2H$ is reasonably estimated. The barrier for the $CF_2 + H$ addition reaction is predicted to be small. In general, this barrier is predicted to be

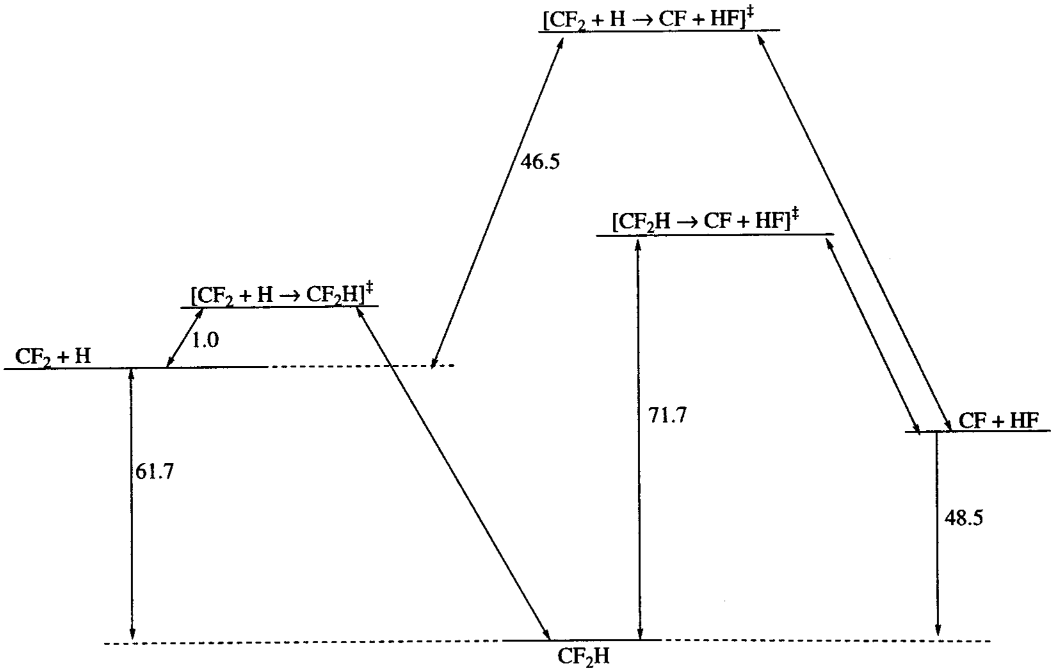

**Figure 2.** Potential energy surface for the $CF_2 + H$ reaction. The values are from the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory.

larger at the MP2 level than the CCSD(T) level of theory. At the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory, the barrier is essentially small, i.e., 1.0 kcal mol$^{-1}$.

*3. 1,1-HF Elimination from $CF_2H$ Radical.* The transition state for the 1,1-HF elimination reaction is depicted in Figure 1b. In the transition state, both the CF′ and CH bonds are elongated. These bonds are 37.4% and 13.8%, respectively, at the corresponding bonds in $CF_2H$. The HF′ is 31.7% of the bond in HF at the CCSD(T)/6-311G(2df,2p) level of theory. The F′CH angle for the 1,1-HF elimination transition state is predicted to be 41.1° at the CCSD(T)/6-311G(2df,2p) level of theory. This angle differs by 1° between CCSD(T) and MP2 levels of theory. The transition state is also characterized by one imaginary frequency, i.e., 1808i cm$^{-1}$. The heat of reaction for the 1,1-HF elimination process is estimated as 48.5 kcal mol$^{-1}$ endothermic at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory. The barrier for the process is estimated at 71.7 kcal mol$^{-1}$ at the same level of theory. It is interesting to note that the MP2 and CCSD(T) barriers are consistent and within 5 kcal mol$^{-1}$ of each other, although the MP2 thermodynamics are overestimated by about 7.5 kcal mol$^{-1}$ in the worst case relative to the best CCSD(T) level of theory.

*4. Summary of the Potential Energy Surface for the $CF_2$ + H Reaction.* There are two pathways for the production of the products, CF + HF, from the $CF_2 + H$ reaction. A summary of the energetics for these pathways is given in Figure 2. The first pathway involves direct abstraction of fluorine. For this pathway, the barrier is quite high, i.e., 46.5 kcal mol$^{-1}$. It is unlikely that it is a dominant pathway in the room temperature reaction studies. The more probable pathway involves the addition of hydrogen to $CF_2$ radicals to form the $CF_2H$ intermediate complex, which dissociates into CF + HF by a 1,1-HF elimination process. We find that the $CF_2 + H$ addition reaction has a small activation barrier of 1.0 kcal mol$^{-1}$ at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory. However, further reaction of the $CF_2H$ radicals to products CF + HF is the limiting reaction step. The barrier for the $CF_2H$ 1,1-HF elimination reaction is 71.7 kcal mol$^{-1}$. This is 9 kcal mol$^{1}$ above the $CF_2 + H$ addition barrier.

There has been a recently published shock-tube study in which the potential energy surface for the $CF_2 + H$ reaction was studied using G2 theory. Yamamori et al.[27] found that the three-center elimination channel was the most energetically favored channel. They also found that, at the G2 level of theory, the direct abstraction barrier is higher than the three-center elimination channel by 35.4 kcal mol$^{-1}$. We find that the direct abstraction channel is 36.5 kcal mol$^{-1}$ higher than the three-center elimination channel. The two results are in good agreement. Moreover, at the G2 level, the transition state for the three-center channel is 10.8 kcal mol$^{-1}$ higher than that of the $CF_2 + H$ reaction, which is consistent with the value of 10.0 kcal mol$^{-1}$ obtained at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G(2df,2p) level of theory reported in this work. A probable conservative uncertainty in the barrier is ±4 kcal mol$^{-1}$ at the CCSD(T)/6-311++G(3df,3pd)//CCSD(T)/6-311G-(2df,2p) level of theory. Yamamori et al. similarly conclude that the formation of CF and HF results from the three-center elimination reaction from $CF_2H$ radicals.

If we assume that, for the $CF_2 + H$ reaction, the preexponential factor is roughly gas-kinetic ($2.5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) at room temperature, the Tsai and McFadden[12] rate of $3.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ yields a barrier of about 1.1 kcal mol$^{-1}$. The Ryan and Plumb[11] rate of $1.6 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ results in a barrier of about 4.3 kcal mol$^{-1}$. Burgess et al.[28] report an activation barrier of 1.2 kcal mol$^{-1}$ for the overall barrier for the $CF_2 + H \rightarrow CF + HF$ reaction. The Burgess estimated barrier is consistent with the Tsai and McFadden[12] measurement. Our present calculations suggest that the overall barrier for the $CF_2 + H \rightarrow CF + HF$ reaction is higher than the 1 kcal mol$^{-1}$ barrier implied by the Tsai and McFadden[12] measurements or the Burgess et al.[28] reported values. The shock-tube studies of Yamamori et al.[27] measured an overall barrier of 4.5 ± 1.6 kcal mol$^{-1}$, consistent with the data of Ryan and Plumb.[11] The present calculation supports the recent measurements of Yamamori et al. and those of Ryan and Plumb.

## IV. Conclusion

The potential energy surface for the $CF_2$ + H reaction has been examined using second-order Møller−Plesset perturbation and coupled cluster methods. The barriers are found to be overestimated with the second-order Møller−Plesset perturbation, compared with the coupled cluster method. Both methods suggest that the most probable mechanism for the $CF_2$ + H reaction is the formation of $CF_2H$ radicals in an addition step, followed by three-centered HF elimination, to produce CF and HF products.

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