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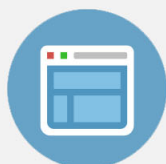J. Chem. Phys. **128**, 104317 (2008); 10.1063/1.2837801

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Dynamics of the F$_2$+CH$_3$SCH$_3$ reaction: A molecule-molecule reaction without entrance barrier

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The F$_2$+CH$_3$SCH$_3$ reaction was studied with crossed molecular beam techniques and high level *ab initio* calculations. Significant reactivity was observed even at low collision energies, consistent with the negligible barrier height obtained from the *ab initio* calculations. All experimental findings are consistent with a weakly bound reaction intermediate of F$-$F$-$S(CH$_3$)$_2$ structure, which possesses a special type of three-center four-electron bonding. Analogous intermediates can also explain the reactions of F$_2$ with CH$_3$SH and CH$_3$SSCH$_3$. © *2007 American Institute of Physics*.
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A molecule with a closed-shell electronic structure is usually believed to be more stable than a radical with an open-shell electronic structure. This common knowledge is often referred to as the *octet rule*; it has been used with great success to predict the stability of many chemical species over decades. In comparison with radical reactions, much weaker reactivity and higher activation energies are expected for reactions between two closed-shell molecules. Here, we report a type of reaction that violates this general rule: we found that the reaction between F$_2$ and CH$_3$SCH$_3$ has a negligible activation barrier despite the closed-shell nature of both reactants. In all previous investigations of interactions between F$_2$ and closed-shell molecules (e.g., I$_2$, ICl, HI, CH$_3$I, C$_2$H$_4$, and C$_6$H$_6$) in crossed molecular beams, a considerable collision energy was required to promote a reaction.[1–8] Of many reactions of F$_2$ with closed-shell molecules, the rate constants were found to be much smaller than those of corresponding F$_2$ reactions with radical species.[9] However, an extraordinarily large rate constant of $(1.6 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was observed at room temperature for the F$_2$+CH$_3$SCH$_3$ reaction.[10] It has been speculated[10] that this atypical reactivity correlates with the stability of the ion pair [CH$_3$SCH$_3$]$^+$[F$_2$]$^-$. Although several products have been investigated in bulk by mass spectrometry, infrared emission spectroscopy,[10] and photoelectron spectroscopy,[11] it is hard to deduce the reaction mechanism

due to difficulty of identifying the primary products in the multiple-collision experiments. Moreover, in the absence of high level quantum calculations, the nature of the unusual reactivity remains elusive.

In this work, the crossed molecular beam technique was applied for the first time to investigate the F$_2$+CH$_3$SCH$_3$ reaction. Such single-collision experiments enable one to identify the primary reaction products at well defined collision energies. Two product channels (channels I and II) were directly observed:

I: F$_2$ + CH$_3$SCH$_3$ → HF + CH$_2$S(F)CH$_3$;

II: → F + CH$_3$S(F)CH$_3$.
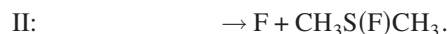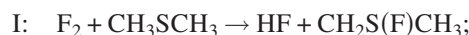
Structures of the products were identified by comparing their photoionization thresholds with the values from *ab initio* calculations. The collision energy dependences of the reaction cross section and branching ratio were studied. Energetics and structures on the reaction paths were calculated with high level *ab initio* methods. A comprehensive and unambiguous reaction mechanism was proposed based on the experimental and computational results.

The experiments were performed with two crossed molecular beam apparatuses: One employed electron impact ionization[12] and the other photoionization.[13] Two reactant beams crossed each other at a 90° angle. The short pulse ($<20~\mu$s) of the F$_2$ beam produced from a fast solenoid valve (Even-Lavie valve, high repetition rate model, $\leqslant 1000$ Hz) (Ref. 14) was used to define the starting time of

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the collision events. Time-of-flight spectra of the scattered products were measured with a time-resolved quadrupole mass spectrometer. Angular distributions of the products were measured on varying the angle between the detector and molecular beams. Synchrotron radiation from the 9 cm undulator beamline[15] of the Taiwan Light Source provided the bright tunable vacuum UV photon beam with intensity of $\sim 10^{16}$ photons/s. Photoionization efficiency spectra of the products were recorded on varying the wavelength of the synchrotron radiation. To transform the data measured in the laboratory (lab) frame to the center-of-mass (c.m.) frame, we used a forward convolution method. The instrument functions, such as velocity spreads of the molecular beams, width of the flight length, etc., and the Jacobian factor of the lab-c.m. transformation are included in the computer program. In some experiments, CD_3SCD_3 (99% D, Aldrich, Inc.) was used in order to shift the masses of the products, and thus to avoid the background from impurities of the commercial CH_3SCH_3 sample (99%, Aldrich, Inc.). We did not observe any significant isotope effect in this study, including the reaction thresholds, angular distributions, product photoionization spectra, etc. Although in many cases it is unnecessary, the impurity contribution from the CH_3SCH_3 sample can be subtracted on performing $Ar+CH_3SCH_3$ scattering experiments under similar conditions. For the determination of the relative reaction cross section at various collision energies, the CH_3SCH_3 beam intensity was measured with a fast ionization gauge (Beam Dynamics, Inc.); the F_2 beam intensity was deduced using the attenuation method, in which a reduction of the CH_3SCH_3 beam intensity was caused by collisions with the F_2 molecular beam.

The reaction paths were searched mainly using the complete active space self-consistent field (CASSCF) calculation with the second-order perturbation corrections (CAS-PT2), in which the active spaces were carefully selected and tested. The minimum energy paths were constructed by scanning the reaction coordinate (or a geometry parameter close to the reaction coordinate) from the reactant state to the product state, in which other degrees of freedom were optimized. The zero-point energy was calculated with the CAS-PT2 method. For singlet structures, the geometry optimization and zero-point energies can be checked with quadratic configuration interaction [QCISD(T)] calculations. Single-point energies were obtained with CCSD(T) (couple cluster) calculations with a complete basis set extrapolation scheme, in which Dunning's cc-pVTZ (triple zeta), cc-pVQZ (quadruple zeta), and cc-pV5Z (quintuple zeta), basis sets were used on the S and F atoms. The quality of basis sets was found to be important for the S and F atoms, but not crucial for the C and H atoms (the results from cc-pVDZ and cc-pVTZ basis sets are very similar; cc-pVDZ basis sets were used on the C and H atoms in most cases). The basis set superposition error was checked with the counterpoise method. This error becomes insignificant when using cc-pVQZ or larger basis sets. The calculations were performed with the MOLPRO 2006.1 quantum chemistry package.[16]

Two sulfur-containing species with masses of 80 [identified as $CH_2{=}S(F){-}CH_3$] and 81 [identified as $CH_3{-}S(F){-}CH_3$] were detected as nascent products. The
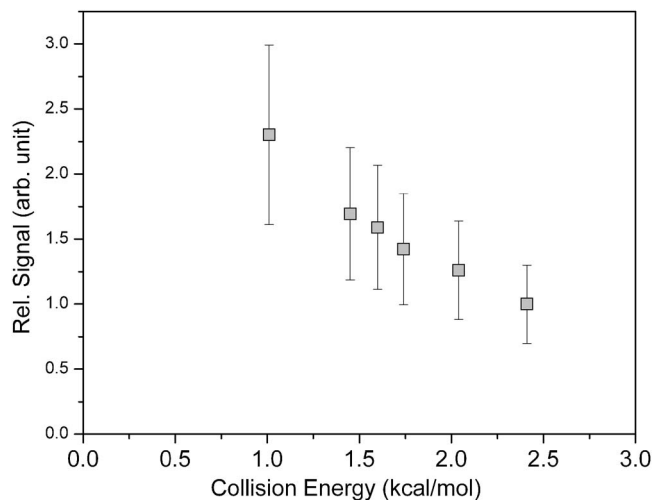

FIG. 1. The relative reaction cross section of channel I as a function of collision energy. The relative signal intensity has been normalized with respect to the F_2 and CH_3SCH_3 beam intensities.

photoionization efficiency spectra were recorded with the synchrotron radiation facilities for both products to discriminate between possible isomers. The ionization thresholds of the products with masses of 80 and 81 were determined to be 8.7 ± 0.1 and 7.8 ± 0.1 eV, respectively. The computed adiabatic ionization energy (IE) for two most likely isomer products with the mass of 80, $CH_2{=}S(F){-}CH_3$ and $CH_2F{-}S{-}CH_3$, were found to be 8.59 and 9.09 eV, respectively, with the CCSD(T) method. We noticed that fluorine substitution in the methyl group of CH_3SCH_3 (IE $=8.70$ eV) increases its ionization energy by about $+0.4$ eV. A similar effect has been observed previously for chlorine substitution ($CH_2Cl{-}S{-}CH_3$, IE$=9.08$ eV).[17] The isomer $CH_2F{-}S{-}CH_3$ has clearly too high ionization energy to match the observed photoionization threshold, hence the major product with mass of 80 can be assigned as $CH_2{=}S(F){-}CH_3$, supported by agreement between the observed and calculated IEs. For product with mass of 81, its ionization threshold is 0.9 eV less than that of CH_3SCH_3. A structure corresponding to $CH_3{-}S(F){-}CH_3$ is the most reasonable assignment for this mass with the vertical IE calculated to be 7.89 eV. This finding is consistent with an intermediate species observed in a previous flow-tube experiment,[11] in which the vertical IE was measured to be 8.03 eV with photoelectron spectroscopy and tentatively assigned to the above structure.

Channel I is highly exothermic, with calculated $\Delta H^{\circ}_{0\text{ K}}$ equal to -80.6 kcal/mol. Its products, $HF+CH_2S(F)CH_3$, were observed to have high translational energy ($\sim 25\%$ of the available energy is deposited into the translational degrees of freedom). The experimental cross section of channel I did not show any significant decrease when we gradually tuned down the collision energy from 11 to 1 kcal/mol. In fact, it increases for lower collision energies, as shown in Fig. 1. Thus, the barrier of this reaction is expected to be much lower than 1 kcal/mol, otherwise, we should see a decline in signal when reducing the collision energy. In contrast, the signal of channel II vanished for low collision energies and increased rapidly for high energies (Fig. 2). To
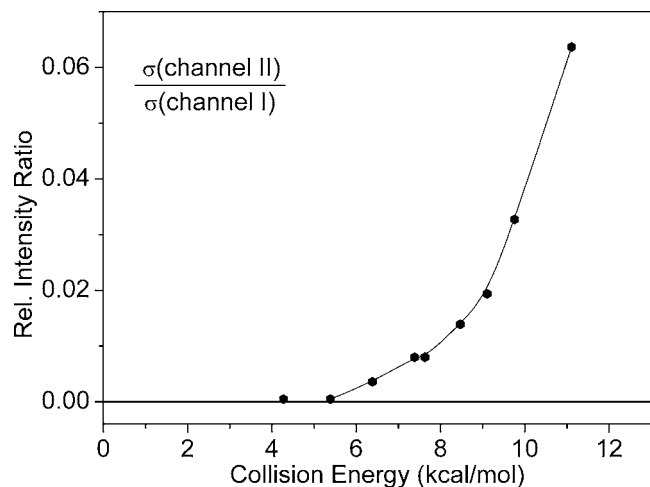
FIG. 2. Relative intensity (branching) ratio of product channel II/I as a function of collision energy. These data were obtained by analyzing the time-of-flight spectra of products CD_3SFCD_3 and CD_2SFCD_3 in the crossed beam reaction of $F_2+CD_3SCD_3$. The corresponding results obtained from the $F_2+CH_3SCH_3$ reaction yield a similar curve but with a higher background.

FIG. 4. Optimized structure of $SF_2(CH_3)_2$ [by QCISD(T)/cc-pVDZ(H,C) and cc-pVTZ(S,F)].

determine the threshold of channel II more precisely, we measured the velocity spreads of the molecular beams and calculated the spread of the collision energy to be ±0.7 kcal/mol (± half width at half maximum). Then, we can perform the deconvolution and determine the threshold for channel II to be 6.0±0.7 kcal/mol.

Neither reaction channel shows a forward-backward symmetric angular distribution, a typical signature of a reaction with a long-lived intermediate.[18] Both sulfur-containing products exhibit significantly forward angular distributions (with respect to the velocity of the CH_3SCH_3 reactant). This finding indicates that the time scale of the reaction is substantially shorter than one rotational period of the collision complex.

To understand the reaction mechanism, high level *ab initio* calculations were performed. In the entrance region, a transition state (TS1 in Fig. 3) was found and characterized using the CAS-PT2 and CCSD(T) calculations. From analysis of the CASSCF molecular orbitals near the transition state region, we found that the interaction originates mostly
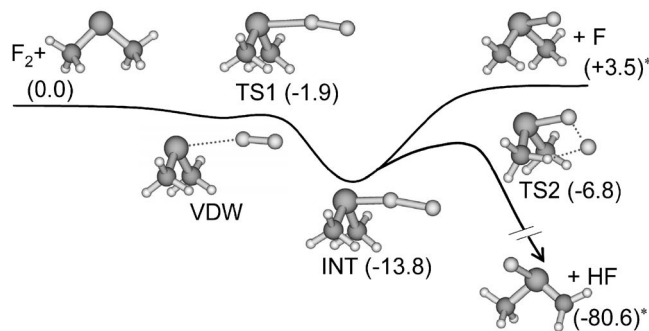

FIG. 3. Optimized structures for the van der Waals entrance well (VDW), transition states (TS1, TS2), intermediate (INT), and products are shown on schematic reaction paths. Relative energies (in kcal/mol), calculated using the CCSD(T) method with complete basis set extrapolation, are given in parentheses for each structure. Numbers denoted with * include zero-point energy corrections.
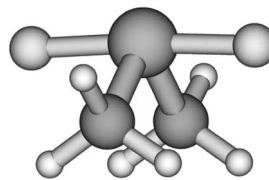
from the coupling between the $3p_z$ orbital of sulfur and the $2p_z$ orbital of fluorine. Based on both experimental and computational results, we propose the following reaction mechanism. In the entrance region, the preferred geometry leading to reaction has a roughly linear F–F–S structure; the axis connecting these atoms (the z axis) is approximately perpendicular to the C–S–C molecular plane. After passing a negligible barrier (TS1), an intermediate (INT) may be formed. Being weakly bound, the outer F atom is quite floppy. If the collision energy is sufficiently large, this atom can dissociate directly on breaking the $F-FS(CH_3)_2$ bond. Another pathway—with the outer F atom bending toward the methyl group and eventually forming HF product—predominates, however, driven by its lower barrier (TS2) and a large reaction exothermicity. At the CCSD(T) and CAS-PT2 levels of theory, the energies of TS1 and TS2 are lower than the energy of the reactants and the zero-point energy corrections are found to be insignificant (<0.6 kcal/mol). That is, both high level *ab initio* methods predict that there is no activation barrier for channel I, an unusual finding for reactions between two closed-shell molecules.

For the reaction to occur, INT is the key structure, in which the F–F–S bonding has a special three-center four-electron character.[19] From analysis of the CASSCF molecular orbitals, we found that two electrons from the S lone pair and two electrons from the F_2 σ bond are distributed in the three active orbitals of the F–F–S bonding (consisting mainly of the $2p_z$-$2p_z$-$3p_z$ orbitals, respectively) at the structure of INT. Structures other than INT can also be imagined and calculated. If both F atoms are directly attached to the S atom of CH_3SCH_3, a structure with nearly collinear F–S–F bonds can be formed [$SF_2(CH_3)_2$ in Fig. 4]. This structure is similar to SF_4 molecule and is, in fact, much more stable than INT. However, migration of the outer F atom of INT to the opposite side is kinetically unfavorable. If this very stable structure is formed, its lifetime should be much longer than that of INT and thus the product angular distribution should be symmetric. Besides HF formation, the decomposition of $SF_2(CH_3)_2$ probably produces $CH_3+SF_2(CH_3)$, a quite exothermic channel. In fact, these evidences of forming $SF_2(CH_3)_2$ cannot be found in the experiments, suggesting that it hardly competes with the two reaction paths shown in Fig. 3.

$CH_3S(F)CH_3$ is an intriguing open-shell species; the calculated dissociation energy of the $F-S(CH_3)_2$ bond is 33.4 kcal/mol, which is only slightly weaker than the dissociation energy of F_2 ($D_{0,calc}=36.7$ kcal/mol, $D_{0,expt}=36.9$ kcal/mol). Hence, channel II is slightly endothermic. Because the preferred impact direction of F_2 does not coincide with the center of mass of the CH_3SCH_3 molecule, the

experimental threshold of channel II should be corrected in order to compare with the calculated enthalpy of reaction. The direction of reactive F_2 collisions is roughly perpendicular to both C–S bonds. The two methyl groups can thus be regarded as spectators along the reaction path of channel II. The effective collision energy for the F_2–S interaction can be expressed approximately as

$$E_{\text{eff}} = \frac{\mu(\text{F}_2 - \text{S})}{\mu(\text{F}_2 - \text{CD}_3\text{SCD}_3)} E_c = 0.71 E_c, \qquad (1)$$

where μ is the reduced mass of the relevant collision partners and E_c is the conventional collision energy. The remaining 29% of E_c is transferred mostly into the centrifugal energy of the collision complex. The experimental threshold of 6.0 ± 0.7 kcal/mol should be scaled down with Eq. (1), yielding the value of 4.3 ± 0.5 kcal/mol. Then, the experimental bond dissociation energy of $\text{F}-\text{S}(\text{CH}_3)_2$ can be deduced as $36.9 - 4.3 = 32.6$ kcal/mol.

Crossed molecular beam reactions of F_2 with other organosulfur compounds ($\text{CH}_3\text{SH}, \text{CH}_3\text{SSCH}_3$) are under investigation. As expected, similar results were observed for the $F_2 + \text{CH}_3\text{SH}$ reaction. More interesting results were obtained for the $F_2 + \text{CH}_3\text{SSCH}_3$ reaction. The major product channel was observed to be $\text{CH}_3\text{SF} + \text{CH}_3\text{SF}$, whereas a minor channel, $\text{F} + \text{CH}_3\text{SS}(\text{F})\text{CH}_3$ (an analog to channel II), could be detected for collision energies greater than 4 kcal/mol. Similar to the $F_2 + \text{CH}_3\text{SCH}_3$ reaction, high reactivity at low collision energies (~ 1.5 kcal/mol) was observed. We consider that the reaction mechanism described above is also applicable to explain these results. We surmise that, after forming a similar intermediate, the outer F atom reacts preferentially with the other S atom forming a four-member ring structure, eventually leading to breaking of both S–S and F–F bonds. On the other hand, we have found that the reactions of F_2 with simple alkenes (C_2H_4 and C_3H_6) revealed quite different features: (a) much higher collision energy is required to observe the reaction products; (b) only one product channel producing $\text{F} + \text{C}_n\text{H}_{2n}\text{F}$ was observed. The $\text{HF} + \text{C}_n\text{H}_{2n-1}\text{F}$ product channel was not found; (c) the corresponding angular distributions are backward biased, indicating that small impact parameter collisions are required to overcome the activation barriers.[18] The interaction of F_2 with the C=C double bond shows typical behaviors of a direct reaction with a significant barrier—an interesting comparison to the above F_2+organosulfur reactions that feature a negligible barrier and a short-lived intermediate. Finally, we contend that the above proposed mechanism is generally applicable for reactions of F_2 with molecules having loosely bound lone-pair electrons.

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