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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$_3$.

A molecule with a closed-shell electronic structure is usually referred to as the open-shell electronic structure. This common knowledge 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±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:

\begin{align*}
\text{I:} & \quad \text{F}_2 + \text{CH}_3\text{SCH}_3 \rightarrow \text{HF} + \text{CH}_3\text{S(F)CH}_3; \\
\text{II:} & \quad \rightarrow \text{F} + \text{CH}_3\text{S(F)CH}_3.
\end{align*}

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 ps) of the F$_2$ beam produced from a fast solenoid valve (Even-Lavie valve, high repetition rate model, \approx 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 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$_3$SCD$_3$ (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$_3$SCH$_3$ 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$_3$SCH$_3$ sample can be subtracted on performing Ar+CH$_3$SCH$_3$ scattering experiments under similar conditions. For the determination of the relative reaction cross section at various collision energies, the CH$_3$SCH$_3$ 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$_3$SCH$_3$ 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 energy was calculated with the CAS-PT2 method. The minimum energy paths were constructed by scanning the reaction coordinate corresponding to CH$_2$F–S–CH$_3$ has clearly too high ionization energy to mediate species observed in a previous flow-tube experiment, in which the vertical IE was measured 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=S(F)–CH$_3$ and CH$_2$F=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$_3$SCH$_3$, (IE=8.70 eV) increases its ionization energy by about +0.4 eV. A similar effect has been observed previously for chlorine substitution (CH$_3$Cl=S–CH$_3$, IE=9.08 eV). The isomer CH$_2$F=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=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$_3$SCH$_3$. A structure corresponding to CH$_3$S=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, 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 \( \Delta H^0_K \) equal to \(-80.6 \) kcal/mol. Its products, HF+CH$_3$S(F)CH$_3$, were observed to have high translational energy (\(-25\% \) 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
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. From analysis of the CASSCF molecular orbitals, we found that two electrons from the F$_2$ 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.
The effective collision energy for the $F_2$–$S$ interaction can be expressed approximately as

$$E_{\text{eff}} = \frac{\mu(F_2 - S)}{\mu(F_2 - CD_3SCD_3)} E_c = 0.71 E_c,$$

(1)

where $\mu$ 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 $F$–$S$ 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, $\text{F}+\text{CH}_3\text{SS}(F)\text{CH}_3$ (an analog to channel II), could be detected for collision energies greater than 4 kcal/mol. Similar to the $F_2$+$\text{CH}_3\text{SSCH}_3$ reaction, high reactivity at low collision energies ($\sim 1.5$ 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 ($\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$) revealed quite different features: (a) much higher collision energy is required to observe the reaction products; (b) only one product channel producing $\text{F}+\text{C}_2\text{H}_2\text{F}$ was observed. The $\text{HF}+\text{C}_2\text{H}_2\text{F}$ 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. The interaction of $F_2$ with the $\text{C}==\text{C}$ 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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