Barrierless Reactions between Two Closed-Shell Molecules: Dynamics of F_2+CH_3SCH_3 Reaction

Yu-Ju Lu (呂育儒)[1], Lance Lee (李久林)[1], Jun-Wei Pan (潘俊維)[2], Henryk A. Witek[2], and Jim Jr-Min Lin (林志民)[1]

[1]Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan
[2]Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

It is a widely accepted concept that radicals are more reactive than molecules, especially for molecules of closed-shell electronic character. Mechanistic studies of elementary reactions between two closed-shell molecules are much more challenging, mostly due to small reaction rate constants. As a result, in the literature there are very few investigations of mechanism of molecule-molecule reactions, in contrast to numerous studies of radical-molecule reactions. We have demonstrated an unusual type of chemical interaction between two closed-shell molecules, F_2 and CH_3SCH_3 (dimethyl sulfide; DMS). Two primary product channels have been identified with the crossed molecular beam technique:

I: $F_2 + CH_3SCH_3 \rightarrow HF + CH_2{=}S(F){-}CH_3$,
II: $\rightarrow F + CH_3{-}S(F){-}CH_3$,

The reaction enthalpies of these channels are: H^o_{0K} (I) = -80.1 kcal/mol and H^o_{0K} (II) = 3.4 kcal/mol.

Two sulfur-containing species with mass = 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 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 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 isomers of the mass 80 product, $CH_2{=}S(F){-}CH_3$ and $CH_2F{-}S{-}CH_3$, were found to be 8.59 eV 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). *J. Chem. Phys. 114, 4817 (2001)*. The isomer $CH_2F{-}S{-}CH_3$ has clearly too high an ionization energy to match the observed photoionization threshold, hence the major product of mass 80 can be assigned as $CH_2{=}S(F){-}CH_3$, supported by agreement between the observed and calculated IE.

For this reaction, the collision energy dependences of the reaction cross section and branching ratio have been investigated. All experimental results are consistent with the model of a weakly bound $F{-}F{-}S(CH_3)_2$ intermediate, which possesses a special type of three-center four-electron bonds. Remarkably, this intermediate can be formed without activation energy. A clear evidence for this conclusion is that the experimental cross section of channel I increases when the collision energy is reduced. On the other hand, collision energy larger than 6 kcal/mol is needed for observing the products of the endothermic channel II.

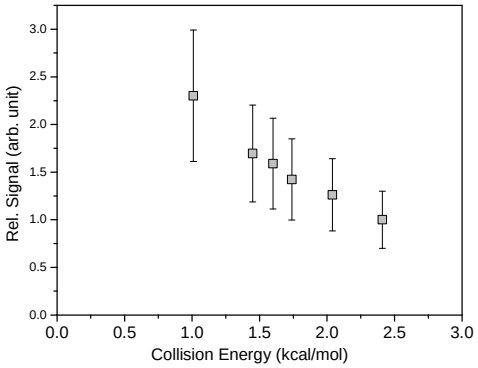

Figure 1. The relative reaction cross section of Channel (I) as a function of collision energy. J. Chem. Phys. 127, 101101 (2007)

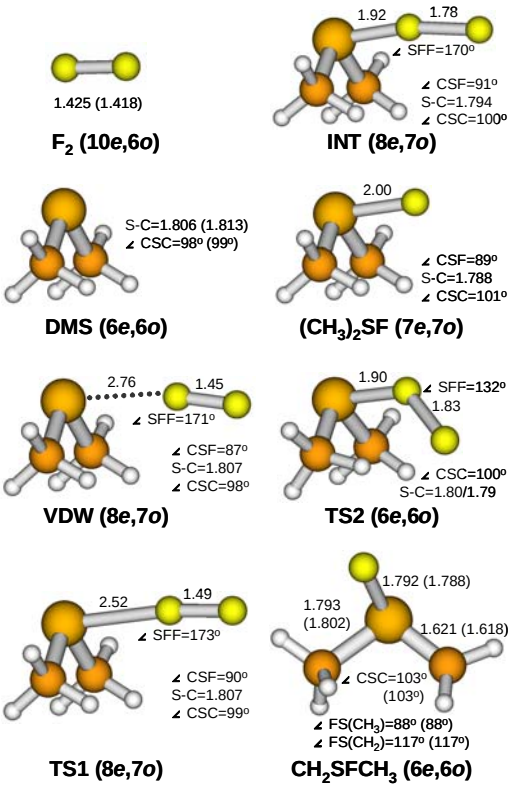

Figure 2. Optimized CASPT2 structures of F_2, DMS, van der Waals entrance well (VDW), transition states (TS1, TS2), intermediate (INT) and products. Selected bond distances (in Å) and angles (in degrees) are shown. The active spaces used in each optimization are denoted as (ne, mo) [n electrons distributed in m orbitals]. The QCISD(T) values (if applicable) are shown in parenthesis. Lu et al. J. Chem. Phys. Accepted (2008).