

Dynamics of Crossed-Beam Reaction $C(^3P) + SiH_4$

Shih-Huang Lee (李世煌)¹, I-Chung Lu (盧聰中)²,
Wei-Kan Chen (陳偉侃)¹, and Wen-Jian Huang (黃文建)¹

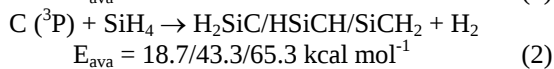
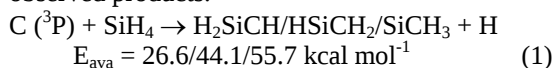
¹National Synchrotron Radiation Research Center, Hsinchu, Taiwan

²Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

The reactions of atomic C with H_2/D_2 , CH_4 , C_2H_2 , C_2H_4 , C_3H_6 , hydrocarbon radicals, etc. have received much attention in experimental and theoretical investigations because the chemistry of atomic carbon is important in combustion, atmosphere, interstellar space and fundamental research. The reaction of atomic C with SiH_4 (silane) might play an important role in the chemical-vapor deposition (CVD) of silicon carbide (SiC).

In one source chamber equipped with a solenoid valve (Even-Lavie) and a discharge device, C atoms were generated from CO molecules with high-voltage pulses. A mixture of 3% CO + 97% He was employed as a discharge medium to produce C atoms. We applied electrical pulses (-1 kV and 10 μ s) to the inner electrode and grounded the outer electrode of the discharge device; the discharge produced dissociation of CO when pulses of gas traversed the gap between the electrodes. In the other source chamber equipped with an Even-Lavie valve and a skimmer we generated a collimated discrete beam of silane of diameter ~ 3 mm in the reaction region. Atomic carbon and silane have most probable velocities 1780 m s⁻¹ and 820 m s⁻¹ at stagnation pressures 100 psi and 70 psi, respectively, so that $E_c = 4.0$ kcal mol⁻¹. The source assembly is rotatable from $\Theta = -20^\circ$ to 110° with regard to the TOF axis; Θ denotes the laboratory angle between the atomic beam and the detection axis.

In the crossed molecular-beam apparatus, we measured the TOF spectra of products with $m/z = 43$ and 42. The following two reactions are responsible for the observed products.



With a simulation program 'XBEAM' based on forward convolution we fitted the angle-specific TOF spectra of products with kinetic-energy distributions $P(E_t; \theta)$ and an angular distribution $T(\theta)$; E_t is the total kinetic energy of two momentum-matched products and θ is the scattering angle of a product with respect to the incident direction of C-atoms in the center-of-mass (c.m.) frame.

With ionizing photons at energy 7.7 eV, we measured the TOF spectra of product $H_2SiCH/HSiCH_2/SiCH_3$ at eleven laboratory angles (Θ) from 25° to 75° ; the left panels of Fig. 1 present six TOF spectra for products with $m/z = 43$. Near Θ_{cm} , the TOF spectrum at selected angles has a large intensity and a bimodal distribution. The satisfactory speed ratio of atomic carbon reactants makes possible the observation of the bimodal feature. The rapid and slow features correspond to the parts scattered forward and backward to the

detector in the c.m. frame. Away from Θ_{cm} , the TOF distribution becomes unimodal and the signal becomes weak.

We employed computer program XBEAM to mimic the angle-specific TOF spectra with inputs of two trial functions – the distribution $P(E_t)$ of kinetic energy and the angular distribution $P(\theta)$ of products in the c.m. frame. The correlation between release of kinetic energy and scattering angle θ is negligibly weak. E_t is the total kinetic energy of two momentum-matched products. θ , ranging from 0° to 180° , is the scattering angle of products with respect to the direction of incident C atoms in the c.m. frame. After iterative forward convolution, the best simulations are shown in the left panels of Fig. 1 with the experimental data; shown in the right panels of Fig. 1 are the corresponding $P(E_t)$ and $P(\theta)$. The release of kinetic energy shows a small E_t to be preferred with a maximal probability at 6 kcal mol⁻¹ but extending to 35 kcal mol⁻¹, which yields an average kinetic energy 10.5 kcal mol⁻¹. The maximal release of kinetic energy is below the energetic limits of Reactions (1b) and (1c) but above that of Reaction (1a). The angular distribution has a contrast factor $I(0^\circ \text{ or } 180^\circ)/I(90^\circ) \sim 1.3$. The data of products $H_2SiC/HSiCH/SiCH_2$ from reaction (2) are neglected in this short report.

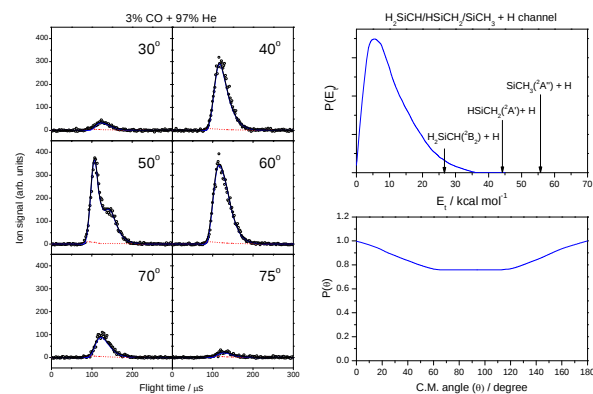


Fig. 1: Left panels present the TOF spectra of species with $m/z = 43$ detected at laboratory angles $30^\circ - 75^\circ$ using photoionization energy 7.7 eV. Open circles denote experimental data; solid and dotted lines denote simulations of products $H_2^{28}SiCH/H^{28}SiCH_2/^{28}SiCH_3$ and $H_2^{29}SiCH/H^{29}SiCH/^{29}SiCH_2$, respectively. A thin solid line represents a sum of the solid and dotted lines. Upper right panel presents the c.m. kinetic-energy distribution and lower right panel the c.m. angular distribution of product $H_2SiCH/HSiCH_2/SiCH_3$ from Reaction (1). Arrows indicate the energetic limits of three isomeric products.