Dynamics of Crossed-Beam Reaction N(^{2}D) + SiH_4

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To model the chemistry of atomic nitrogen in the atmosphere and combustion systems, rate coefficients of many nitrogen reactions and the related photo-dissociations have been measured. A nitrogen atom has three low-lying electronic states ^{4}S, ^{2}D and ^{2}P; the electronic energy of state ^{2}D is 2.38 eV, and of state ^{2}P is 3.576 eV, above that of ground state ^{4}S. In laboratories N atoms are commonly produced from N_2 molecules in an electric discharge either at high voltage or driven at radio or microwave frequencies; outside the zone of the discharge N atoms typically populate the lowest three electronic states ^{4}S, ^{2}D and ^{2}P, with N_2 molecules in the two lowest electronic states X $^1\Sigma_g^+$ and a $^3\Sigma_u^+$.

In one source chamber equipped with a solenoid valve (Even-Lavie) and a discharge device, N atoms were generated from N_2 molecules with high-voltage pulses. A mixture of 3% N_2 + 97% He was employed as a discharge medium to produce N atoms. We applied electrical pulses (-1 kV and 10 μs) to the inner electrode and grounded the outer electrode of the discharge device; the discharge produced dissociation of N_2 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 1830 m s^{-1} and 820 m s^{-1} at stagnation pressures 100 psi and 70 psi, respectively, so that E_c = 4.7 kcal mol^{-1}. The source assembly is rotatable from $\Theta = -20^o$ to 110^o with regard to the TOF axis; Θ denotes the laboratory angle between the atomic beam and the detection axis.

We observed ion signals at m/z = 42 – 45 in the present work. The following reactions might be responsible for the observed products.

$$N(^2D) + SiH_4 \rightarrow H_3SiN/H_2SiNH/HSiNH_2 + H \quad (1)$$
$$\rightarrow HSiNH/SiNH_2 + H + H \quad (2)$$
$$\rightarrow H_2SiN/HSiNH/SiNH_2 + H_2 \quad (3)$$
$$\rightarrow HSiN/HNSi + H_2 + H \quad (4)$$

Product HSiN/HNSi from Reaction (4) was observed at m/z = 43 and product $HSiNH/SiNH_2$ from Reaction (2) at m/z = 44. The signal at m/z = 42 is attributed to daughter ions of those two products, and at m/z = 45 to ^{29}Si and ^{30}Si isotopic variants. We measured TOF spectra of reaction products at 8–10 laboratory angles to derive differential cross sections – the distribution of kinetic energy P(E_t,θ) and the angular distribution P(θ) of products. With a simulation program XBEAM based on a forward convolution and taking into account uncertainties of experimental parameters, including velocity spreads and divergences of reactants and the ionization length, we mimicked TOF spectra $N_{lab}(t, \Theta)$ using P(E_t,θ) and P(θ). Because the yields of fragments H and H_2 are below the detection limits, we can not solve exactly the triple fragmentation problems for Reactions (2) and (4). We assume in the present analysis that Reactions (2) and (4) are binary dissociations with mass ratios 44:2 and 43:3, respectively. Although the present analysis omits some detailed reaction dynamics, the resultant P(E_t,θ) and P(θ) might reflect the kinetic-energy and angular distributions, respectively, of detected products.

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(θ) 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^o to 180^o, is the scattering angle of products with respect to the direction of incident N 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(θ). The release of kinetic energy tends to a small E_t with a maximal probability at 4 kcal mol^{-1}. The average release $\langle E_t \rangle$ of kinetic energy is 7.7 kcal mol^{-1}, reflecting that products have an average internal energy 22.5 kcal mol^{-1}. The maximal release of kinetic energy is below the energetic limits of $SiNH_2$ + H + H but above that of HSiNH + H + H. The data of products HSiN/HNSi from reaction (4) are neglected in this short report.

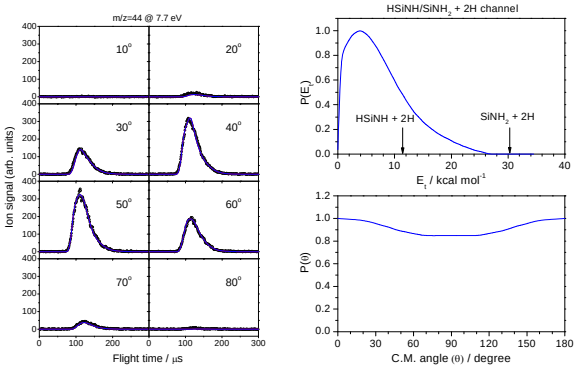

Fig. 1: Left panels present the TOF spectra of species with m/z = 44 detected at laboratory angles 10^o – 80^o using photoionization energy 7.7 eV. Open circles denote experimental data and solid curves the simulations. Upper right panel presents the c.m. kinetic-energy distribution and lower right panel the c.m. angular distribution of product $HSiNH/SiNH_2$ from Reaction (2). Arrows indicate the energetic limits of three isomeric products.