

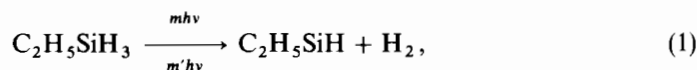
RESEARCH NOTE

Multiple pathways for the direct formation of SiH₂
from the photodissociation of ethylsilaneby C. GONZALES, H. B. SCHLEGEL
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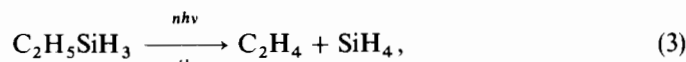
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The reaction of ethylsilane to products C₂H₆ and SiH₂ is calculated to go via two different reaction pathways to the same products by using a reaction path following method. The difference in the two pathways is the orientation in which SiH₂ dissociates; the implications for reaction dynamics are discussed.

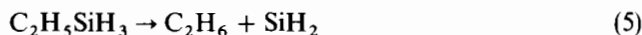
Silylene (SiH₂) has been identified as a key intermediate in the decomposition of silicon hydrides [1-3] and organosilanes [4-6]. Infrared multiple-photon dissociation (IRMPD) of alkylsilanes has been found to be a good source of SiH₂ [7-10]. However, production of SiH₂ by IRMPD is suggested not to be a result of primary photolysis of the organosilane, but rather as a consequence of secondary IRMPD of the substituted silylene. The mechanism that describes the source of SiH₂ from ethylsilane (C₂H₅SiH₃) occurring by secondary dissociation is either



or



On the basis of molecular orbital calculations [11], reactions (1) and (2) comprise the more probable mechanism for SiH₂ formation. The possibility of producing SiH₂ by primary photodissociation of ethylsilane via a three-centre elimination, reaction (5), has also been explored computationally; it was found that there are two distinct



reaction pathways which lead to the products ethane and silylene. The optimized transition states are shown in figure 1. One transition state, structure A, resembles the usual transition state for SiH₂ addition across a CH bond; while the other, structure B, appears to correspond to hydrogen shift from SiH₃ to C₂H₅. A full vibrational analysis of these transition states revealed that indeed both structures

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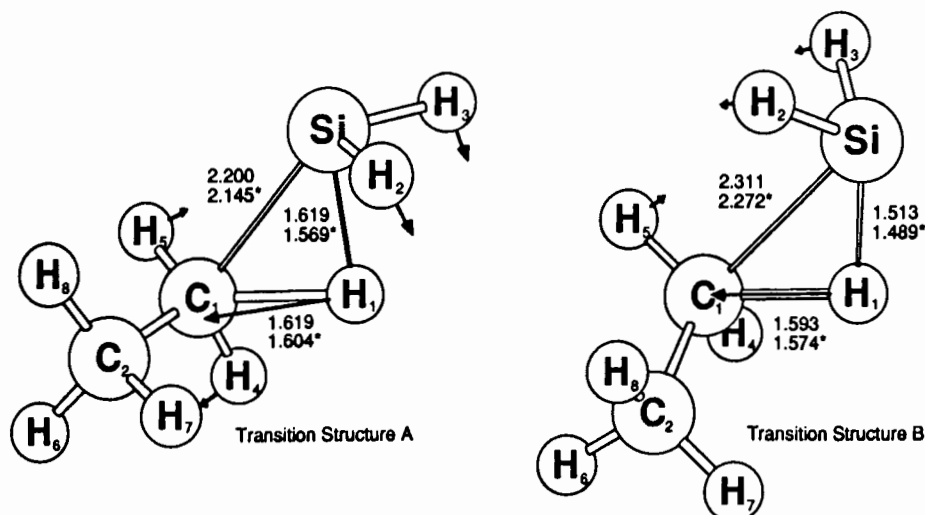


Figure 1. Optimized transition state structures for dissociation of $C_2H_5SiH_3$ to products SiH_2 and C_2H_6 .

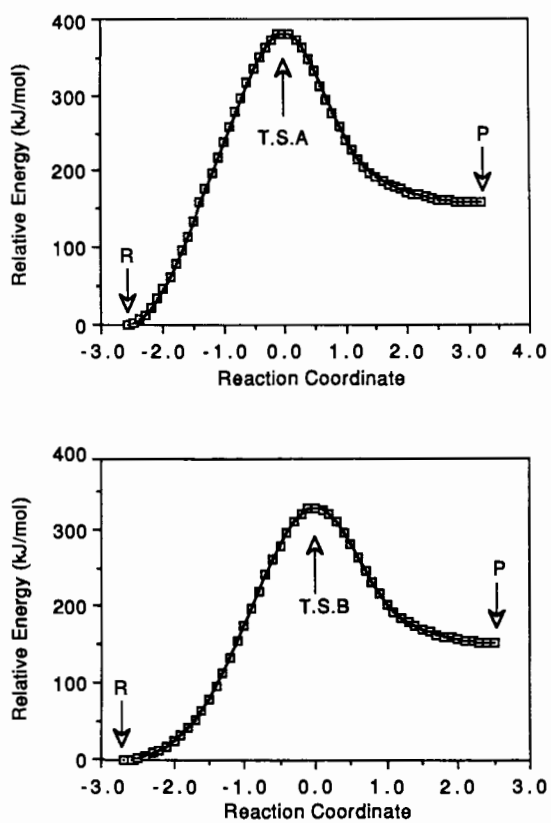


Figure 2. The potential energy as a function of the reaction coordinate for Structure A and Structure B. (R denotes reactant, $C_2H_5SiH_3$, TS denotes the transition state, and P denotes the products, SiH_2 and C_2H_6).

are first order saddle points. Structure *B* was found to be energetically lower than structure *A* by *ca.* 42 kJ mol⁻¹. In examining these results, it is not immediately obvious from either the transition state structure or the orientation of the transition vector whether the transition state connects ethylsilane to the products, SiH₂ and C₂H₆. To this end we have examined these two pathways in more detail to ascertain whether both pathways are indeed true reaction pathways to the same products.

The corresponding reaction paths connecting structures *A* and *B* with reactants and products were determined by using a reaction path following scheme proposed by Gonzalez and Schlegel [12]. Reaction paths connecting structures *A* and *B* (shown in figure 1) with reactants and products were obtained at the HF/3-21 G level using the GAUSSIAN 86 package of programs [13] and the reaction path following algorithm [12] in internal coordinates (bohr, radians) without mass weighting.

Figure 2 shows the complete reaction pathway for both structures *A* and *B* connecting the reactants (C₂H₅SiH₃) and products (C₂H₆ + SiH₂). The heats of reaction for C₂H₅SiH₃ going to the products C₂H₆ + SiH₂ for both structures agree with the HF/3-21 G value of 166.5 kJ mol⁻¹ obtained from the relative energetics of the separated products [11]. Figure 2(a) shows the reaction pathway for structure *A*. The barrier height for this pathway is calculated to be 395.7 kJ mol⁻¹ of the HF/3-21 G level. The present calculation confirms that the transition state structure *A* does lie along a reaction pathway for the formation of SiH₂ + C₂H₆. This is also true for structure *B*, as shown in figure 2(b), but the barrier height for the pathway is lower in energy by *ca.* 42 kJ mol⁻¹. These calculations reveal a fork at the entrance channel for the unimolecular dissociation of ethylsilane to products C₂H₆ and SiH₂.

By examining the transition vectors for the transition states shown in figure 1, one would expect the SiH₂ to dissociate in somewhat different orientations. With the reaction pathway following method, we can map how the SiH₂ proceeds along the reaction pathway to its final dissociation products. Figure 3 shows the optimized geometries of the final products for both structures. As one can clearly see, the products are the same except for the orientation of the species SiH₂. We have examined several points along the path connecting structures *A* and *B* with the corresponding dissociation products. These points reveal, in the case of the path involving structure *A*, that the species SiH₂ is rotating clockwise with respect to the Si-H bond coming out of the plane of figure 3(a). In the case of the path involving structure *B*, the molecule SiH₂ rotates counterclockwise with respect to the Si-H bond pointing towards the plane of figure 3(b).

These data suggest the possibility of two different rotational distributions. One would expect that the differences between the maxima of these distributions will correspond to the energy difference between the two transition states, but it may be difficult to observe these two distributions provided we simply look at the relative populations, since the fraction of SiH₂ produced by channel *A* is much lower than channel *B* (*ca.* 0.003 as obtained from RRKM calculations). In experiments on the infrared multiple-photon dissociation of ethylsilane and n-butylsilane followed by laser-induced fluorescence (LIF) of SiH₂ [8, 9], a large range of rotational states of SiH₂ are found to be populated. It may be that some of these states may have resulted from the SiH₂ coming from the C₂H₆ + SiH₂ dissociation channels, which is a one-step, but of less importance, photolysis channel. In fact, one does observe

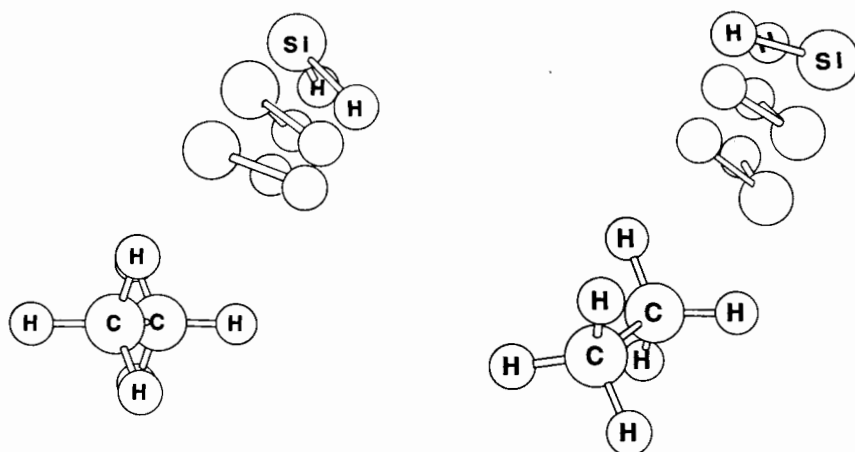


Figure 3. Change of the optimized geometries along the reaction path from the transition state to the final products.

yields of C_2H_6 in these studies to be ≤ 10 per cent [7]. Consequently, it may be the case that the wide range of observed rotational states of SiH_2 is due to the fact that SiH_2 comes from both primary (reaction (5)) and secondary (reaction (2)) photolysis of ethylsilane. The subtleties in the potential energy surfaces for the reaction leading to $C_2H_6 + SiH_2$ cannot be distinguished by IRMPD/LIF experiments.

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References

- [1] SCOTT, B. A., PLECENIK, R. M., and SIMONYI, E. E., 1981, *Appl. Phys. Lett.*, **39**, 73.
- [2] SCOTT, B. A., BRODSKY, M. H., GREEN, D. C., KIRBY, D. B., PLECENIK, R. M., and SIMONYI, E. E., 1981, *Appl. Phys. Lett.*, **37**, 725.
- [3] ERWIN, J. W., RING, M. A., and O'NEAL, H. E., 1985, *Int. J. chem. Kinet.*, **17**, 1067.
- [4] MAZAL, C. J., and SIMONS, J. W., 1968, *J. Am. chem. Soc.*, **90**, 2482.
- [5] RING, M. A., O'NEAL, H. E., RICKBORN, S. F., and SAWREY, B. A., 1983, *Organometallics*, **2**, 1891.
- [6] RICKBORN, S. F., RING, M. A., and O'NEAL, H. E., 1984, *Int. J. chem. Kinet.*, **16**, 1372.
- [7] FRANCISCO, J. S., JOYCE, S. A., STEINFELD, J. I., and WALSH, F., 1984, *J. phys. Chem.*, **88**, 3098.
- [8] THOMAN, J. W., Jr, and STEINFELD, J. I., 1986, *Chem. Phys. Lett.*, **124**, 35.
- [9] RAYNER, D. M., STEER, R. P., HACKETT, P. A., WILSON, C. L., and JOHN, P., 1986, *Chem. Phys. Lett.*, **123**, 449.
- [10] FRANCISCO, J. S., and STEINFELD, J. I., 1987, *Spectrochimica Acta A*, **43**, 207.
- [11] FRANCISCO, J. S., and SCHLEGEL, H. B., 1988, *J. chem. Phys.*, **88**, 3736.
- [12] GONZALEZ, C., and SCHLEGEL, H. B., *J. chem. Phys.* (submitted).
- [13] FRISCH, M. J., BINKLEY, J. S., DEFREES, D. J., RAGHAVACHARI, K., SCHLEGEL, H. B., WHITESIDE, R. A., FOX, D. J., MARTIN, R. L., FLUDER, E. M., MELIUS, C. F., KAHN, L. R., STEWART, J. J. P., BOBROWICZ, F. W., and POPLE, J. A., 1984, *GAUSSIAN 86*, Carnegie-Mellon (Quantum Chemistry Publishing Unit).