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Theoretical Investigation for the Abstraction Reaction of H with $(CH_3)_3GeH$

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Abstract: The abstraction reaction of H atom with $(CH_3)_3GeH$ has been studied using *ab initio* molecular orbital theory. The kinetics calculation has been deduced using the canonical variational transition state theory (CVT) with the small-curvature tunneling correction method (SCT) over the temperature range of 200-3000 K. The CVT/SCT rate constants exhibit typical non-Arrhenius behavior, and a three-parameter rate-temperature formula has been fitted as follows: $k=6.66\times10^{-18}T^{2.33}\exp(-60.3/T)$ (in units of cm^3 $molecule^{-1}$ s^{-1}).

Keywords: Trimethylgermane, *ab initio* calculation, variational transition state, rate constants.

The reaction of H atom with $(CH_3)_3GeH$ is considered to play important role in chemical vapor deposition (CVD) processes used in the semiconductor industry [1-2]. The reaction mechanism and kinetics nature for this reaction are therefore essential input data for computer-modelling studies directed towards obtaining an understanding of the factors controlling CVD processes. However, despite its importance, the kinetics work about this reaction was very limited. Only two groups studied experimentally this reaction. In 1977, Austin [3] measured the rate constants of this reaction using an indirect method. In 1998, Arthur [4] obtained an Arrhenius expressions using direct method: $k=(8.80\pm1.09)\times 10^{-11}\exp(-929\pm45)/T$ for the reaction of H with $(CH_3)_3GeH$. To our best knowledge, little theoretical attention has been paid to this reaction. In this paper, we have initiated a theoretical study of the application of *ab initio* electronic calculations combined with the variational transition state theory for the reaction of atomic H with $(CH_3)_3GeH$.

Computational Methods and Theory

Ab initio calculations have been carried out using Gaussian 94 programs[5]. The geometries and the frequencies of the reactant, transition states and products have been optimized at the MP2/6-31G(d) level. The G2MP2 theory has been used in the final single-point energy calculation. The rate constants were calculated using the variational transition state theory with the small curvature tunneling effect correction. All the kinetical calculations have been carried out using the Polyrate 7.8 program [6].

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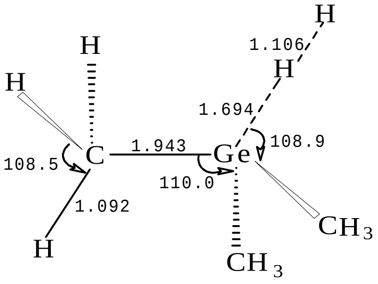
Result and Discussion

Reaction mechanism

The reaction of H with $(CH_3)_3GeH$ can proceed *via* two channels: the hydrogen abstraction from the Ge-H bond and the hydrogen abstraction from the C-H bond. A good approximation for the rate constants attack on the methyl groups can be obtained by considering the rate constants of the reactions of H with $(CH_3)_4Si$ and $(CH_3)_4Ge$. At 305 K, Austin and Lampe found both reactions to be too slow to measure, but a rate constant can be evaluated from the Arrhenius parameters for $(CH_3)_4Si$ reported by Potzinger[7]. The value at 298 K is 1.15×10^{-16} cm^3 $molecule^{-1}$ s^{-1}. Adjusting for the number of the C-H bonds in the different germanes, Arthur evaluated the rate constant of attack on C-H bonds to be less than 0.002% of the experimental value[8] at room temperature for the reaction of H with $(CH_3)_3GeH$. The barrier height calculated at the G2MP2 level is 2.21 kcal/mol for the hydrogen abstraction from the Ge-H bond, while the barrier height of the hydrogen abstraction from the C-H bond is 11.74 kcal/mol. The latter is much higher than the former. Thus, we can safely say that attack on the methyl groups in the trimethylgermane is negligible, which is similar to the mechanism of the reaction of H with $(CH_3)_3SiH$. Therefore, we mainly discuss the hydrogen abstraction reaction from the Ge-H bond.

Figure 1 MP2/6-31G(d) optimized geometries for the transition state



Distance is in Å and angle is in degree

The geometrical parameters of the transition state calculated at the MP2/6-31G(d) level are shown in **Figure 1**. For this hydrogen abstraction reaction from the Ge-H bond, the H atom attacks linearly the H of the Ge-H bond, and the transition state has C_{3V} symmetry. The breaking Ge-H bond is elongated by 8.31%, while the forming H-H bond is longer than the equilibrium value 0.738 Å in H_2 by 49.86%. Therefore, the transition state is reactant-like, and the hydrogen abstraction reaction from $(CH_3)_3GeH$ proceeds *via* early transition state. This rather early character in the transition state is in accordance with the low potential barrier and the high exothermicity of the title reaction. The transition state has one and only one imaginary frequency (1581i cm^{-1}). The value of the imaginary frequency is large, which implies that the quantum tunneling effect may be significant and may play an important role in the calculation of the rate constants.

The kinetics calculation

The canonical variational transition state theory (CVT) with a small curvature tunneling correction (SCT), which has been successfully performed for several analogous reactions, is an effective method to calculate the rate constants. In this paper, we used this method to calculate the rate constants for the reaction of H with $(CH_3)_3GeH$ over a wide temperature range from 200 to 3000 K. The calculated CVT/SCT rate constants along with the experimental values are shown in **Figure 2** for this title reaction. The calculated TST and CVT are also depicted in **Figure 2** for comparison purposes. Several important features of the calculated rate constants are following:

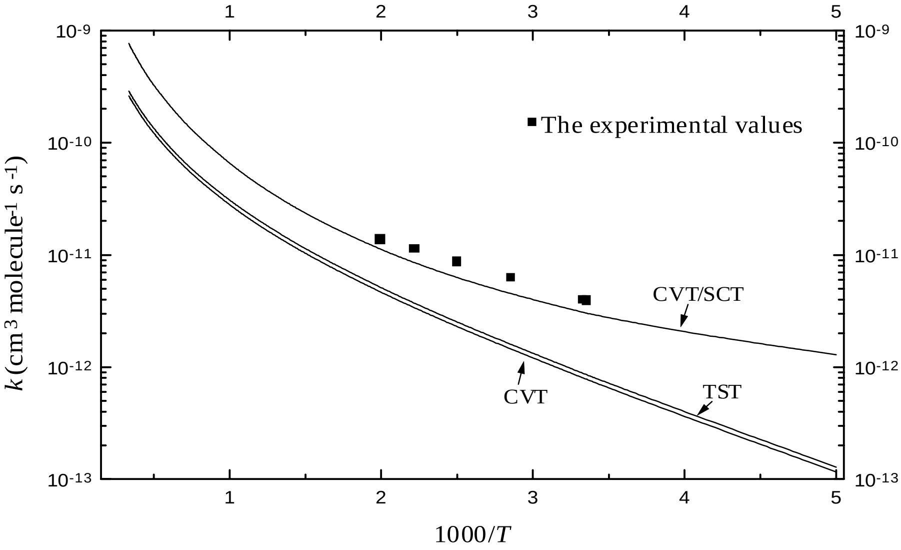
(1) It can be seen that the values of TST rate constants and those of CVT rate constants are nearly the same, which enables us to conclude that the variational effect is small for this reaction.

(2) The CVT rate constants are much smaller than those of CVT/SCT, especially in the lower-temperature range, which means that the quantum tunneling effect is significant. For example, at 298 K, the CVT rate constant is 7.73×10^{-13} cm^3 molecule^{-1} s^{-1}, while the CVT/SCT rate constant is 3.01×10^{-12} cm^3 molecule^{-1} s^{-1}. The latter is 3.89 times larger than the former. At 1000 K, the CVT rate constant is 2.78×10^{-11} cm^3 molecule^{-1} s^{-1}, while the CVT/SCT rate constant is 6.52×10^{-11} cm^3 molecule^{-1} s^{-1}. The latter is 2.35 times larger than the former.

(3) The calculated CVT/SCT rate constants are in excellent agreement with the experimental values over the temperature range of 298-500 K. For example, at 298 K, the CVT/SCT rate constant is 3.01×10^{-12} cm^3 molecule^{-1} s^{-1}, while the experimental value is 3.90×10^{-12} cm^3 molecule^{-1} s^{-1}. At 500 K, the CVT/SCT rate constant is 1.11×10^{-11} cm^3 molecule^{-1} s^{-1}, while the experimental value is 1.37×10^{-11} cm^3 molecule^{-1} s^{-1}. Therefore, the CVT/SCT method is a good choice to calculate accurate rate constants for the title system. Both TST and CVT methods underestimate the rate constants.

(4) It is obvious that the CVT/SCT rate constants exhibit typical non-Arrhenius behavior. A three-parameter formula is fitted as follows (in units of cm^{3}molecule^{-1}s^{-1}):
$k=6.66\times10^{-18}T^{2.33}\exp(-60.3/T)$

Figure 2 Rate constants as function of the reciprocal of the temperature (*T*) in the temperature range of 200-3000K for the reaction of H with $(CH_3)_3SiH$



Acknowledgments

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