

A Theoretical Study on Nonadiabatic Trapping Models of the Reaction NH+H \leftrightarrow N+H₂

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Abstract: The properties of nonadiabatic trapping models of the reaction NH+H \leftrightarrow N+H₂ are investigated in a collinear model as well as a non-collinear thermal reaction on the basis of the intrinsic reaction coordinate (IRC) information obtained by *ab initio* calculations at QCISD/6-311G** level. Using the unified statistical theory for nonadiabatic trapping models, the thermal rate constants over the temperature range of 2000-3000 K are computed which are in excellent agreement with the experiment results.

Keywords: Intrinsic reaction coordinate (IRC); unified statistical theory (UST); nonadiabatic trapping model; thermal rate constant.

The hydrogen atom transfer reaction NH+H \leftrightarrow N+H₂ is an important reaction in radical reactions and the gas-phase thermal decomposition of ammonia. There were several studies on this reaction in experiment¹ and theory^{2,3}. In this paper, we have employed the unified statistical theory⁴ (UST) to study the detailed dynamics of this reaction.

As one of the microcanonical variational models, UST combines the direct and complex mechanism into unit, and is especially used for the nonadiabatic trapping model. The latter has no potential well on the potential energy surface (PES), but shows multi-dividing surfaces along PES because of the entropic effect. The dividing surfaces are located by searching the relative minima or relative maxima of the microcanonical flux integral $N_s(E)$ on PES. Due to the difficulty of obtaining entire PES, we have provided an approach⁵ to apply UST only based on the information of the intrinsic reaction coordinate (IRC) instead of the total PES. The thermal rate constant for a reaction system in UST can be expressed as:

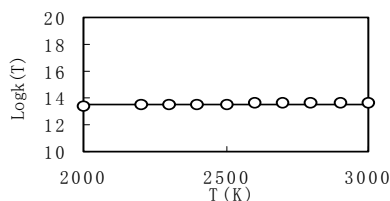
$$k(T) = [hQ(T)]^{-1} Q_t^\ddagger(T) \int_0^\infty \frac{N_1(E)N_2(E)}{N_1(E) + N_2(E) - N_1(E)N_2(E)/N_x(E)} \times \exp(-E/k_bT) dE$$

where $Q(T)$, $Q_t^\ddagger(T)$ are the partition function of reactants and the translational partition function of the transition state, respectively; $N_1(E)$, $N_x(E)$ and $N_2(E)$ are the vibrational-rotational flux integral through the dividing surface S_1 , S_x and S_2 , which correspond to the relative minimum, maximum and minimum of $N_s(E)$ along IRC, respectively.

The properties of the reactants, products, the transition state and IRC are computed at QCISD/6-311G** level. $N_s(E)$ is calculated by using the method of counting the number of quantized states⁶. In order to shed light on the factors that affect the distribution of the dividing surfaces, we investigated the reaction as both a collinear model and a non-collinear thermal reaction.

The calculated $N_s(E)$ shows that, (1) for the collinear model, multiple minima of $N_s(E)$ appear and the property of nonadiabatic trapping model is noticeable, which is caused mainly by the strong variance of the bound stretching vibrational frequency along IRC; (2) the non-collinear reaction shows little character of nonadiabatic trapping model because the effects of the other two degenerate bending vibrations on $N_s(E)$ are opposite to one of the stretching vibration. In the non-collinear reaction, the minimum of $N_s(E)$ moves from $S=0.0$ to around $S=0.4$ with the energy increase and there are unnoticed multi-minima and an unobtrusive relative maximum of $N_s(E)$ in the energy region of 14-20 kcal/mol.

Figure 1. Calculated (circles) and experimental (line) rate constants for $\text{NH}+\text{H}\leftrightarrow\text{N}+\text{H}_2$. The unit of $k(T)$ is $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$.



According to the locations and distribution of the dividing surfaces, the integral energy range is divided into several subintervals. By using our previous method⁶, the thermal rate constants for the no-collinear reaction over the temperature range of 2000-3000 K are calculated. The calculated results given in **Figure 1** agree well with the experimental ones.

Acknowledgments

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