

INFLUENCE OF THE ESSENTIAL FEATURES OF THE POTENTIAL  
ENERGY SURFACE ON THE TEMPERATURE DEPENDENCE OF THE  
 $\text{H} + \text{CH}_3 \rightarrow \text{CH}_4$  REACTION

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Microcanonical statistical adiabatic channel model calculations show that the temperature dependence of the limiting high pressure rate coefficients of the title reaction becomes less positive (or more negative) when the attractiveness of the radial or the attenuation of anisotropic parts of the potential energy surface increases.

Расчеты модели микроканонического статистического адиабатического канала свидетельствуют о том, что температурная зависимость лимитирующего коэффициента скорости при высоком давлении для заглавной реакции становится менее положительной (или более отрицательной) с увеличением притяжения радиальной или затухания анизотропной частей поверхности потенциальной энергии.

## INTRODUCTION

Recent kinetic data compilations recommend for the limiting high pressure rate coefficient  $k_{\text{rec},\infty}$  of the  $\text{H} + \text{CH}_3$  association reaction a small negative temperature dependence. In fact, the expressions  $k_{\text{rec},\infty} = 1 \times 10^{-7} \text{ T}^{-1}$  between 300-2500 K

## COBOS: POTENTIAL ENERGY SURFACE

and  $2 \times 10^{-9} T^{-0.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  between 300-1000 K have been reported in Refs [1] and [2], respectively. However, we have shown very recently that a constant value  $k_{\text{rec},\infty} = 3.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 300-1000 K gives a very good fit to most reliable association-dissociation data [3,4]. On the other hand, different theoretical approaches have been employed to calculate  $k_{\text{rec},\infty}$  using several potential energy surfaces (PES) [3,5-9]. Contrary to the above recommended data, all these studies predict positive temperature dependences, namely, between  $T^{0.2}$  and  $T^{0.8}$ . In this Letter we present the results of a microcanonical statistical adiabatic channel model (SACM) study on the influence of the relevant PES features on the temperature dependence of  $k_{\text{rec},\infty}$  for the  $\text{H} + \text{CH}_3$  association over the temperature range 200-600 K, in which direct experimental data are available.

### THEORETICAL FORMALISM AND DISCUSSION

In the frame of the SACM [10,11]  $k_{\text{rec},\infty}$  is given, via detailed balance, by the expression

$$k_{\text{rec},\infty} = (1/hK_c Q) \sum_{J=0}^{\infty} (2J+1) \int_0^{\infty} W(E,J) \exp(-E/kT) dE \quad (1)$$

Here  $Q$  denotes the total partition function for  $\text{CH}_4$ ,  $K_c$  the statistically evaluated equilibrium constant, and  $W(E,J)$  the total energy ( $E$ ) and total angular momentum (quantum number  $J$ )-resolved total number of adiabatic open channels for dissociation of a highly excited  $\text{CH}_4$  molecule backwards into  $\text{H} + \text{CH}_3$ .

The central problem in the calculation of  $k_{\text{rec},\infty}$  is the exact counting of  $W(E,J)$ . The number of open channels for the transitional bending modes (TBMs) was obtained by quantum convolution of the twofold degenerate  $\text{H}_3\text{C}---\text{H}$  bending mode with the highest rotational constants of the  $\text{CH}_3$  radical. Subsequently, the Beyer-Swinehart counting algorithm was used to convolute the number of open channels for the TBM together with the conserved oscillators. Finally,  $W(E,J)$  is obtained after correcting by coupling of the angular momentum and

symmetry.  $W(E,J)$  depends sensitively on the radial and angular parts of the PES. Although realistic ab initio PES have been employed in earlier canonical SACM studies of this reaction [6,7], simpler potential functions have been used here to analyze in a transparent way, without loss of generality, the relationship between  $k_{rec,\infty}$  and dominant parameters of the PES. For this, the radial  $H_3C-H$  potential was modeled with a standard Morse function  $V(r)=D_e\{1-\exp[-\beta(r-r_e)]\}^2$ , where  $D_e$  is the  $H_3C-H$  bond dissociation energy,  $r$  the interfragment distance and  $\beta$  the Morse parameter. Besides, potential anisotropy effects were accounted for by interpolating the channel eigenvalues with the relationship  $S(r)=\exp[-\alpha(r-r_e)]$ ,  $\alpha$  being a looseness parameter. TBMs coupling was treated as detailed earlier [11]. Further details can be found elsewhere [10,11].

The interplay between the  $\beta$  and  $\alpha$  potential parameters determines the absolute value and the temperature dependence of  $k_{rec,\infty}$ . In order to analyze the role that the range of the attractive potential plays, we have fixed a value  $\alpha = 13.0 \text{ nm}^{-1}$  while  $\beta$  changes between 23.5 and 26.0  $\text{nm}^{-1}$ . For each  $\beta$ - $\alpha$  pair five  $k_{rec,\infty}$  values were calculated between 200-600 K with eq. 1 and fitted with the expression  $k_{rec,\infty} = A(T/300)^n$  (mean correlation coefficient = -0.993). As Table 1 shows, the calculations predict negative temperature coefficients  $n$  which become more negative when the attractiveness of the potential rises. Recent ab initio calculations show that at the relevant  $H_3C-H$  bond elongations, 0.35-0.45 nm, the electronic potential can be very well described by a Morse function with  $\beta = 25.0(\pm 0.5) \text{ nm}^{-1}$  [12]. Therefore, taking this  $\beta$  value, the influence of the attenuation of the TBMs during the reaction  $k_{rec,\infty}$  was investigated. Table 1 also shows the  $k_{rec,\infty}$  values obtained changing the  $\alpha$  parameter between 10.0 and 16.0  $\text{nm}^{-1}$ . It can be seen that when the TBM attenuation increases, the calculated  $k_{rec,\infty}$  values rise notably and  $n$  decreases, being  $n < 0$  for  $\alpha > 12.0 \text{ nm}^{-1}$ . Results similar to those given in Table 1 were obtained using other alternative

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Table 1  
 Dependence of A and n on the potential parameters  
 $\beta$  and  $\alpha$  A in units of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  
 $\beta$  and  $\alpha$  in  $\text{nm}^{-1}$

$\beta$	23.5	24.0	24.5	25.0	25.5	26.0	
A	6.14	5.60	5.17	4.74	4.28	3.88	
n	-0.17	-0.16	-0.16	-0.14	-0.12	-0.088	
$\alpha$	10.0	11.0	12.0	13.0	14.0	15.0	16.0
A	1.25	2.02	3.15	4.74	6.40	8.18	9.93
n	0.22	0.095	-0.17	-0.14	-0.17	-0.19	-0.20

formulations for the TBMs coupling [13]. Employing the values  $\beta=25.0 \text{ nm}^{-1}$  and  $\alpha=12.3 \text{ nm}^{-1}$  a  $k_{\text{rec},\infty} = 3.5 \times 10^{-10} (T/300)^{-0.05} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is calculated in very good agreement with our recommended value mentioned above [3,4]. Moreover, in this case, the ratio  $\alpha/\beta=0.49$  agrees very well with the standard value that frequently fits this type of reactions,  $0.46 \pm 0.09$  [14].

It seems to be appropriate at this stage to mention the factors that determine the observed temperature dependence of  $k_{\text{rec},\infty}$ . Along the  $\text{CH}_4$  dissociation, the transformation TBMs-hindered rotations- $\text{CH}_3$  free radical, is described by adiabatic channels which depend parametrically on the reaction coordinate. Each channel has an associate effective potential which is given by additive contributions of the radial potential, the energies of the remanent TBM, the energies of the conserved oscillators, and the centrifugal energy. In this way, the channel eigenvalue for a given TBM depends sensitively on the excitation state of the remaining oscillators and the rotational level of the  $\text{CH}_4$  dissociating molecule. Therefore, when the temperature rises, channels with higher E and J values are populated according to a Boltzmann distribution, and an increase of the internal couplings is expected. As it is demonstrated in Ref. [11], these state-selected mode coupling effects

decrease the effective potential range yielding a contraction of the phase space available to the TBMs larger ( $n$  values smaller) than those predicted by previous theoretical approaches [3,5-9].

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