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STATISTICAL ADIABATIC CHANNEL MODEL CALCULATIONS OF THE REACTION OF H ATOMS AND FO RADICALS ON *AB INITIO* POTENTIAL ENERGY SURFACES

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Abstract

The statistical adiabatic channel model has been used to calculate rate coefficients for the reaction between H atoms and FO radicals on potential energy surfaces based on density functional theory and *ab initio* calculations between 200 and 1000 K. The rate coefficient calculated at 300 K with the *ab initio* potential is in good agreement with a recently reported experimental value.

Keywords: Rate coefficient, statistical adiabatic channel model, potential energy surface, FO radical

INTRODUCTION

Reactions involving H atoms are of particular importance in many combustion systems [1]. On the other hand, H+radical reactions offer an attractive test for detailed quantum chemical and theoretical kinetics studies against experiments. In this context, the kinetics of the reaction between H atoms and FO radicals has been recently studied in detail in a flow system by monitoring the H, O, F atoms and OH radicals by EPR and the FO by LMR [2]. Two reaction channels have been found to be operative





for which the overall rate coefficient of $k_1 = k_{1a} + k_{1b} = (2.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been determined at 300 K. 66% of the reaction occurs through process (1a).

This Letter is concerned with a theoretical study of reaction (1) employing the statistical adiabatic channel model (SACM) coupled with potential energy surfaces constructed from the results of either density functional theory (DFT) or *ab initio* molecular orbital calculations.

THEORETICAL FORMALISM, RESULTS AND DISCUSSION

Experimental and theoretical evidence supports the relevance of the formation of strongly bound highly vibrationally excited collision complexes in bimolecular reactions such as $\text{O} + \text{OH} \rightarrow \text{HO}_2 \rightarrow \text{H} + \text{O}_2$ and $\text{OH} + \text{CO} \rightarrow \text{HOCO} \rightarrow \text{H} + \text{CO}_2$ [1,3-5]. Similarly, reaction (1) probably proceeds *via* the formation of the energized well-known FOH molecule in the ground electronic state which afterwards dissociates preferentially to OH and F ($\Delta H^0 = -49.8 \text{ kcal mol}^{-1}$ [5]) or isomerizes to HFO to generate HF and O ($\Delta H^0 = -83.9 \text{ kcal mol}^{-1}$ [5]). Both channels are highly exothermic and therefore the collision complex is short-lived enough to be collisionally stabilized. Under these conditions, the capture process determines the overall reaction rate. Rate coefficients for reaction (1) have been evaluated employing the following SACM [6] expression

$$k_1 = (k_B T / h) (h^2 / 2\pi\mu k T)^{3/2} P_{el} (Q_{cent} Q_{bend} Q_{str} F_{AM} / \sigma) / Q_v Q_r \exp(-\Delta E_{0z} / k_B T) \quad (2)$$

In this equation μ is the reduced mass of the system, P_{el} the electronic degeneracy factor, Q_{cent} the centrifugal pseudopartition function, Q_{bend} the transitional partition function for the bending, F_{AM} an angular momentum coupling correction factor, σ the effective activated complex symmetry number, Q_r the rotational partition function of FO and ΔE_{0z} the adiabatic zero-point barrier for the lowest reaction channel. The ratio Q_{str}/Q_v between the vibrational partition functions for F-OH and F-O stretching modes is close to unity. Q_{cent} and Q_{str} are given by

$$Q_m = \sum_{i=0}^{\infty} g_i \exp\{-[E_0(i) - E_0(i=0)] / k_B T\} \quad (3)$$

The degeneracy factor g_i is equal to $2J+1$ in Q_{cent} and equal to one in Q_{bend} . $E_0(i)$ denotes the threshold energy levels derived from the maxima of each adiabatic channel potential

$$V_a(r,i) = V(r) + \hbar \omega_{\text{bend}} S(r) (i+1/2) + B_{\text{FO}} (1-S(r)) i(i+1) + B_{\text{eff}}(r) i(1-S(r)) [i(1-S(r))+1] \quad (4)$$

Here i is the channel number, r the H-OF bond distance, $V(r)$ the electronic potential, $\hbar \omega_{\text{bend}}$ the harmonic vibrational bending frequency, B_{FO} the FO rotational constant, $B_{\text{eff}}(r) = [A(r) + B(r)]/2$ the effective rotational constant and $S(r)$ a switching function employed to represent the smooth evolution of the transitional mode from the free FO rotor to the FOH bending mode along the minimum reaction path.

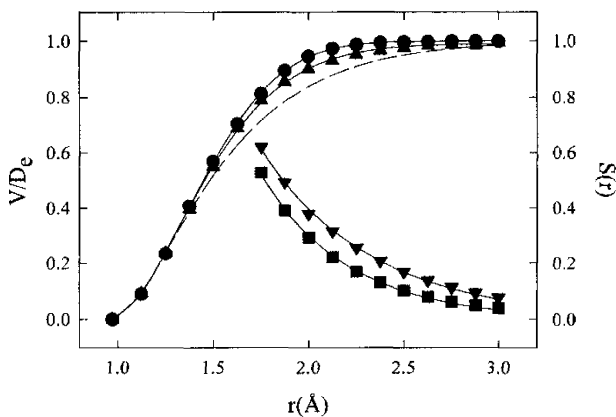


Fig. 1. Dependence of the normalized electronic potentials and the switching functions on the H-OF bond distance. Electronic potentials: (▲) UB3LYP/6-311++G(2d,p) calculations; (●) UCCSD(T)/6-311++G(2d,p)//MP2/6-311++G(2d,p) calculations. The dashed line illustrates a Morse potential calculated with $\beta_{\text{eq}} = 2.41 \text{ \AA}^{-1}$. Switching functions: (▼) B3LYP/6-311++G(2d,p) calculations; (■) MP2/6-311++G(2d,p) calculations. The solid lines are the results of the fits described in the text

$V(r)$, $B_{\text{eff}}(r)$ and $S(r)$ were obtained from two different quantum chemical approaches. In a first calculation, the bending frequencies and energies as functions of the H-OF bond distance were obtained for fully optimized

geometries using the B3LYP hybrid functional [7,8] of the DFT with the 6-311++G(2d,p) basis set. In the second case, *ab initio* geometries and frequencies were calculated at the MP2/6-311++G(2d,p) level of theory while single point energy calculations on these derived geometries were carried out employing the same basis set but using the high correlated coupled cluster singles and doubles approach, including a perturbational estimate of the triple excitations CCSD(T) [9]. The calculated $V(r)/D_e$ and $S(r)=\hbar\omega_{\text{bend}}(r)/\hbar\omega_{\text{bend}}$ ratios are depicted in Fig. 1. All calculations were performed with the Gaussian 98 program [10]. The first ratio was fitted by means of the modified Morse function $V(r)/D_e=\{1-\exp[-\beta(r)(r-r_e)]\}^2$ with $\beta(r)=\beta_{\text{eq}}+a_1(r-r_{\text{eq}})+a_2(r-r_{\text{eq}})^2+a_3(r-r_{\text{eq}})^3$. The values $D_e=101.4$ kcal mol⁻¹, $r_e=0.973$ Å, $\beta_{\text{eq}}=2.34$ Å⁻¹, $a_1=0.13130$ Å⁻², $a_2=0.89503$ Å⁻³, and $a_3=-0.45707$ Å⁻⁴ were employed for the DFT potential while the values $D_e=97.2$ kcal mol⁻¹, $r_e=0.972$ Å, $\beta_{\text{eq}}=2.41$ Å⁻¹, $a_1=-0.58948$ Å⁻², $a_2=2.35351$ Å⁻³, and $a_3=-0.76034$ Å⁻⁴ were used for the *ab initio* potential. A Morse potential calculated with $\beta_{\text{eq}}=2.41$ Å⁻¹ is shown in Fig. 1 for comparison. The switching functions were represented as $S(r)=b \exp(-\alpha r)$ using the values $b=1.80 \times 10^4$ and $\alpha=1.7366$ Å⁻¹ for the DFT calculations ($\hbar\omega_{\text{bend}}=1408$ cm⁻¹) and $b=3.56 \times 10^4$ and $\alpha=2.2237$ Å⁻¹ for the *ab initio* calculations ($\hbar\omega_{\text{bend}}=1394$ cm⁻¹). The centrifugal energies were calculated using the functions $B_{\text{eff}}(r)=c_1/(c_2+c_3 r+c_4 r^2+c_5 r^3)$. The DFT calculations were fitted with $c_1=0.8592$ cm⁻¹, $c_2=1.3902$, $c_3=-0.53211$ cm⁻¹, $c_4=0.20914$ cm⁻² and $c_5=-0.01822$ cm⁻³ and the *ab initio* calculations with $c_1=0.9105$ cm⁻¹, $c_2=1.6526$, $c_3=-0.97209$ cm⁻¹, $c_4=0.43878$ cm⁻² and $c_5=-0.05397$ cm⁻³. Finally, the values $B_{\text{FO}}=19.52$ and 19.46 cm⁻¹ derived respectively from DFT and *ab initio* calculations were employed. Similar SACM calculations based on empirical and *ab initio* potentials can be found elsewhere [6,11-15].

Table 1

Rate coefficients (in units of cm³ molecule⁻¹ s⁻¹) and rigidity factors calculated for reaction (1) using potential energy surfaces based on DFT and *ab initio* calculations

T(K)	DTF		<i>Ab initio</i>	
	k_1	f_{rigid}	k_1	f_{rigid}
200	3.87×10^{-10}	0.096	2.98×10^{-11}	0.15
300	1.73×10^{-10}	0.11	3.29×10^{-11}	0.16
400	1.20×10^{-10}	0.12	3.56×10^{-11}	0.16
500	9.90×10^{-11}	0.13	3.80×10^{-11}	0.17
600	8.85×10^{-11}	0.13	4.03×10^{-11}	0.17
700	8.26×10^{-11}	0.14	4.24×10^{-11}	0.17
800	7.91×10^{-11}	0.14	4.43×10^{-11}	0.17
900	7.70×10^{-11}	0.14	4.62×10^{-11}	0.17
1000	7.56×10^{-11}	0.14	4.79×10^{-11}	0.17

As mentioned above, the aim of this work is to provide a quantitative comparison between the experimental and SACM rate coefficients. The results of the calculations performed from 200 to 1000 K are summarized in Table 1.

The rate coefficient obtained with the DFT potential clearly fails in reproducing the experimental room temperature k_1 value. However, the more accurate *ab initio* based potential leads to a rate coefficient value, which is only 37% higher than the experimental one. This agreement is encouraging because recombination reactions involving H atoms often present rate coefficients higher than $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [1, 11]. Such high results are mainly due to the small μ values, close to unity (see eq. 2). To explore the reasons for the low experimental k_1 value, the rigidity factor $f_{\text{rigid}} = k_1/k_1(\text{PST})$ [11] for the reaction was evaluated. This factor accounts for the decrease of k_1 from its phase space limit high-pressure rate coefficients $k_1(\text{PST})$, exclusively determined by the radial part of the potential [6,16]. Such decrease is due to the contribution of the bending transitional mode. The calculated f_{rigid} values listed in Table 1 are similar to those estimated for other H+radical recombination reactions employing standard Morse potentials and simple exponential switching functions [11]. This fact indicates that the short range of the electronic potential (compare the range of the potentials in Fig. 1) seems to be the responsible for the low experimental rate coefficient.

The k_1 values given in Table 1 show the dominant influence that the features of the potential energy surface play on the temperature dependence of the rate coefficients. In fact, the interplay established between the decrease of the electronic potential and the rise in the bending vibrational frequency along the reaction path (see Fig. 1) determinates the temperature coefficient of k_1 .

The other reaction channel (1b), presents a sufficiently high value for the rate coefficient that precludes an F atom abstraction mechanism by the H atoms. In fact, direct abstraction processes such as the reactions $\text{F}_2\text{O} + \text{H} \rightarrow \text{FO} + \text{HF}$ and $\text{CF}_3\text{OF} + \text{H} \rightarrow \text{CF}_3\text{O} + \text{HF}$, exhibit much lower room temperature rate coefficients. The values 6.7×10^{-15} [17] and $1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18] have been reported for the former and of $3.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [18] for the latter reaction. Therefore, reaction (1b) appears to occur after isomerization of the energized complex, namely $\text{H} + \text{FO} \rightarrow \text{FOH} \rightarrow \text{HFO} \rightarrow \text{HF} + \text{O}$. Preliminary CCSD(T)/6-311++G(2d,p)//MP2/6-311++G(2d,p) calculations predict a transition state for the isomerization pathway with an imaginary frequency of $958i \text{ cm}^{-1}$ located at a barrier $55.2 \text{ kcal mol}^{-1}$ high (zero-point energies included). This barrier is higher than the energy threshold of the barrierless reaction $\text{FOH} \rightarrow \text{OH} + \text{F}$ of $40.7 \text{ kcal mol}^{-1}$ and both values are smaller than the calculated asymptotic H+FO limit of $94.4 \text{ kcal mol}^{-1}$. These results support the proposed formation of an energized FOH molecule that subsequently generates the products of reactions (1a) and (1b). The magnitude of the branching ratio is determined by their respective energy-dependent specific rate constants. A study related to this subject is underway.

In summary, the above mentioned facts support a complex-forming mechanism and the *ab initio* implemented SACM calculations allow to reproduce satisfactorily the overall experimental rate coefficient of reaction (1) without adjustable parameters.

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