

Quantum chemistry and dynamics of the abstraction reaction of H atoms from formaldehyde



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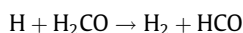
ABSTRACT

This work reports a reduced dimensionality rate constant calculation of the H-abstraction reaction from formaldehyde. Quantum scattering calculations are performed treating explicitly the bonds being broken and formed. Geometry optimisations and frequency calculations are done at the MP2/cc-pVTZ level while energies are calculated with the CCSD(T) method. An analytical potential energy surface was developed from a relatively small number of grid points. When compared to semi-classical approaches, the quantum scattering calculations show that quantum tunnelling yields large contributions at low temperatures. At 200 K, we note a difference of about 5 orders of magnitude between transition state theory (TST) and quantum rate constants. Our predicted results show that the quantum and the CVT/SCT rate constants are in reasonable agreement with the available experiment at high temperatures, but that the last one gives better agreement to experimental results at low temperatures.

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1. Introduction

Aldehydes are major constituents in the troposphere [1,2] and especially formaldehyde is among the most reactive organic contaminants. Due to its thermodynamic stability [3], formaldehyde concentration in the polluted areas of the atmosphere can be relatively important [4]. Moreover, these species are among the most abundant interstellar molecules which can be used to trace local physical parameters [5]. It may result from the reaction of atomic hydrogen with carbon monoxide at low temperature on cold grain surfaces, as proposed by previous experimental works [6]. Once H₂CO is formed, it could be the site of many reactions [6–8,30], including abstraction reaction by hydrogen atom from formaldehyde:



This reaction has been the subject of few experimental studies. The rate constant obtained by Ridley et al. [9] at 297 K is expressed as $5.4 \pm 0.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. The measurements of rate constants by Westenberg and deHass [10] and by Oehlers et al.

[7] were represented by the following Arrhenius expressions $k = 2.24 \times 10^{-11} \exp[-15.71 (\text{kJ/mol})/RT]$ for $297 < T < 652 \text{ K}$ and $k = 1.44 \times 10^{-11} \pm 3.16 \cdot 10^{-12} \exp[(-14.5 \pm 0.7 (\text{kJ/mol})/RT)]$ for $296 < T < 780 \text{ K}$ (in units of $\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$). Friedrichs et al. [8] have studied the high temperature decomposition of CH₂O. The rate constant for H + CH₂O reaction, determined for temperatures ranging from 1510 to 1960 K is expressed as $k = 1.1 \times 10^{-9} \exp[-40.6 (\text{kJ/mol})/RT] \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$. On the theoretical side, Goumans et al. [5] used harmonic quantum transition state theory (HQTST) to predict reaction rates for the gas phase reaction of formaldehyde with hydrogen atoms. In their paper, different isotopic combinations were considered and the abstraction reactions were to be preferred over addition reactions in the case of the following isotopic substitutions H/D + H₂CO.

Since the reaction involves hydrogen atoms, quantum effects (tunneling and variational effects) are expected to be important at low temperatures. Quantum scattering theory allows for an accurate calculation of rate constants and a thorough understanding of state-to-state dynamics of gas phase reactive collisions. However, going beyond three atom systems presents a great challenge for exact quantum dynamical approaches. To overcome these difficulties, a reduced dimensionality quantum scattering method [11,12] has been developed. This approach is based on the idea that only a few degrees of freedom (active modes)

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contribute significantly to the reaction mechanism while the other degrees of freedom can be treated as spectator modes. The current work makes use of a two dimensional (2D) reduced dimensionality (RD) time independent quantum theory based on the combination of (i) accurate *ab initio* calculations to obtain the required effective potential energy surface (PES) and (ii) the quantum scattering method derived from the bending corrected rotating linear model (BCRLM) of Walker and Hayes [13]. Two active modes are treated explicitly in the scattering calculations while an approximative treatment is made for the remaining internal degrees of freedom (3N-8) via addition of rectilinear-projected zero point energies (ZPE) to the potential surface. This reduced dimensionality approach was successfully employed to study the H-abstraction reaction from small molecules like C1–C3 alkanes and methanol [14–17] and recently to spin–orbit non adiabatic transitions [18], n-butane [19], cyclopropane [20] and tetramethylsilane [21].

In order to analyze in details the contribution of quantum effects, we perform also semiclassical tunneling calculations on a ground-state adiabatic minimum energy path (MEP) potential. The rate constants were computed using the conventional transition state theory (TST) [22] with zero curvature tunneling contributions [23] (TST/ZCT) and the canonical variational transition state method (CVT) [24] with small curvature tunneling contributions [25] (CVT/SCT).

This paper is organized as follows. In Section 2, we thoroughly describe the electronic structure calculations and the analytical construction of the PES. In Section 3, some details of the quantum scattering calculations are presented as well as the method used to derive the reaction probabilities and to determine the quantum rate constants. The semi-classical approach based on TST/ZCT and CVT/SCT methods is also given. The results are discussed in Section 4 and compared with the available experimental and theoretical results. Finally, conclusions are given in Section 5.

2. Electronic structure calculations

2.1. Geometry optimization

Equilibrium geometries of the reactants, products and transition state complex are fully optimized at the second order Møller–Plesset perturbation theory level (MP2) [26] with the correlation-consistent polarized valence basis set of Dunning [27], namely cc-pVTZ, using Gaussian 09 [28]. This approach satisfactorily predicts the geometry and the IR spectra [29]. The geometries of reactants, products and transition state for the hydrogen abstraction reaction are listed in Table 1. The interatomic distances and angles are in good agreement with the experimental [31–33] and past theoretical results [34,35]. Denoting by H_a the incoming and by H_b the abstracted H-atom (see Fig. 1(a)), we see that during the hydrogen abstraction reaction, the C– H_b bond at transition

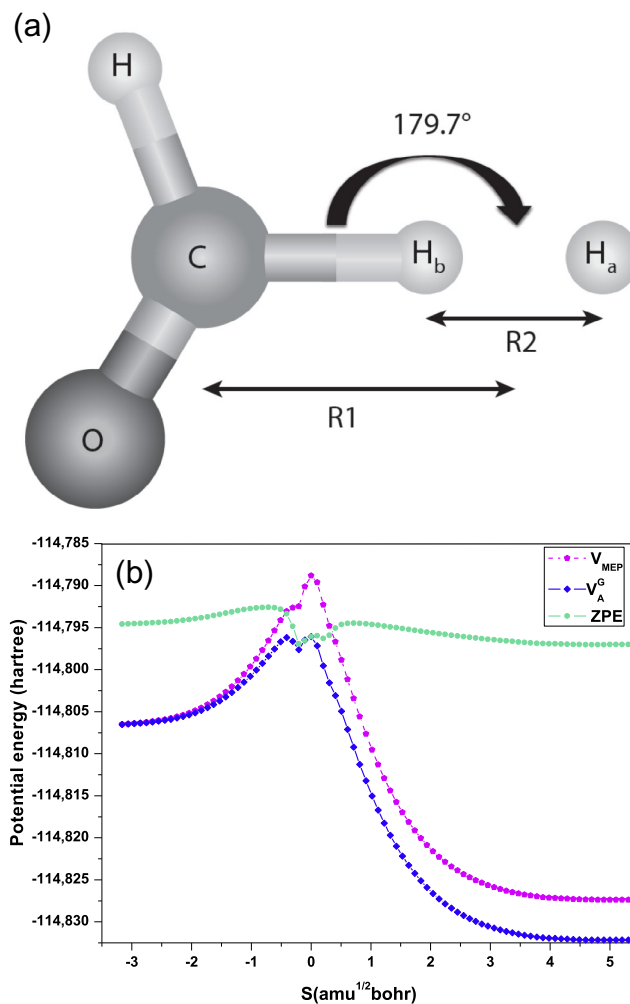


Fig. 1. (a): Optimized geometry of the transition state at the MP2/cc-pVTZ level. The value of the angle involved in the reaction is shown. (b) Minimum energy path (V_{MEP}), vibrational adiabatic potential energy (V_A^C), and ZPE of the 3N-6 vibrational modes as functions of s ($\text{amu}^{1/2} \text{bohr}$) at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level.

state (TS) is longer than the equilibrium value by 15%. Similarly, the H_b – H_a bond formed is longer by about 27% in the activated complex compared to the isolated product. The distance of the C–O bond at the transition state is estimated to be 1.179 Å and is shorter than the bond in the isolated formaldehyde molecule (1.210 Å); this phenomenon was also observed by Henon *et al.* [36] when studying the abstraction reaction of formaldehyde by methoxy radicals. Furthermore, the geometry of TS is almost linear ($\angle \text{C–H–H} = 180^\circ$) (Fig. 1(a)).

Table 1

Molecular geometry parameters of the fragments (bond lengths (Å) and angles ($^\circ$)) at the MP2/cc-pVTZ level. H_b is the abstracted atom, while H_a is the incoming atom.

| Species | Methods/basis | CO | CH | CH_b | $\angle \text{H}_b\text{CO}$ | H_aH_b | $\angle \text{HCH}_b$ | $\angle \text{H}_a\text{CH}_b$ |
|-----------------------|-----------------|-------|-------|---------------|------------------------------|------------------------|-----------------------|--------------------------------|
| H_2CO | MP2/cc-pVTZ | 1.210 | 1.100 | 1.100 | 121.9 | – | 116.1 | – |
| | HF/6-31G**[34] | 1.189 | 1.094 | – | – | – | 116.2 | – |
| | MP2/6-31G**[34] | 1.219 | 1.099 | – | – | – | 115.52 | – |
| | Exp. [31] | 1.203 | 1.099 | – | – | – | 116.5 | – |
| TS | MP2/cc-pVTZ | 1.179 | 1.110 | 1.293 | 125.3 | 1.008 | 112.3 | 179.7 |
| | MP2/cc-pVTZ | 1.182 | 1.117 | – | 124.0 | – | – | – |
| | CCSD/acvqz [35] | 1.176 | 1.118 | – | 124.61 | – | – | – |
| | CCSD/CBS [35] | 1.174 | 1.117 | – | 124.6 | – | – | – |
| H_2 | Exp. [32] | 1.198 | 1.080 | – | 119.5 | – | – | – |
| | MP2/cc-pVTZ | – | – | – | – | 0.737 | – | – |
| R-vdW | Exp. [33] | – | – | – | – | 0.741 | – | – |
| | MP2/cc-pVTZ | 1.210 | 1.100 | 1.100 | 121.9 | 3.351 | 116.18 | – |

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