

The Increase of the Reactivity of Molecular Hydrogen with Hydroxyl Radical from the Gas Phase versus an Aqueous Environment: Quantum Chemistry and Transition State-Theory Calculations

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Abstract. One of the simplest elementary reactions, that between H_2 and OH, is of great theoretical interest in chemical kinetics. Surprisingly it turned out recently to be of importance in medical and biological environments, in search of role of hydrogen as radical scavenger participating in the human body: water is supposed to be of possible influence in this reaction. However, there are no theoretical studies considering solvent effects in the title reaction which in the gas phase is slow. Here, we aim to analyze the H_2 + OH reaction with a blend of electronic structure calculations and the *deformed* Transition-State Theory (*d*-TST) approach. Inclusion of the continuum solvation model density (SMD) was applied for mimicking the role of the aqueous phase. Preliminary results demonstrate an enormous increase in the reactivity between H_2 and OH molecules in water environment, approximately 150- and 138-fold at 25 °C and 36.5 °C, respectively. We expect that these results can help to shed new light on the understanding of the H_2 + OH reaction in aqueous phase, paving the way to research for medical and technological applications.

1 Introduction

The reaction between H_2 and OH molecules is being demonstrated to be of great importance in biological and medical [1] environments, in spite of the simplicity of the molecules participating in the process. The H_2 molecule is the smallest gas molecule

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composed of two protons and two electrons, forming a very stable compound that reacts with the oxide radical ion (O^-) [2]. There are several documentations regarding the antioxidant performance of the H_2 molecule. Studies of selectivity of H_2 molecule in cells inducing oxidative stress and reducing cytotoxicity reactive of oxygenated species, *i.e.*, hydroxyl radical [2–4]. Due to the applicability on the human body, water is supposed to be of great influence in this reaction, however, there are scarce studies from a theoretical viewpoint [5].

The four-body reaction investigation has been propitiated a deep understanding of the mechanism and reactivity of chemical reactions in the gas phase [6–9]. Recently, the prototypical H_2 + OH reaction has been highlighted due to the publication of a paper by Ohsawa et al. [4], which presented results with a significant reduction of cerebral infarction in rats when exposed to of 2% to 4% v/v of molecular hydrogen mixtures. Later works [2, 3, 5, 10–16] obtained promising results in the treatment of 63 types of diseases with the administration of H_2 in several medical areas. The efficacy of the hydrogen molecule was suggested due to neutralization of OH radical [17], in a few cases prejudicial to a living organism, which H_2 has reactive specificity [4]. Concomitantly, this reaction came out to be important in other applications, such as the control of free radicals in the atmosphere [18], gas- and condensed phase reactions [19–21] and photosensitive materials [22]. On another context, the H_2 + OH reaction has been mainly exploited to redirect H_2 gases from nuclear power plants to be reformed. Molecular hydrogen (H_2) has been playing a key role in nuclear power plants since water is used in the refrigeration of reactors with consequent high concentration H_2 and hydrogen peroxide (H_2O_2) formation due water radiolysis – interaction with alpha, beta and gamma radiation [23–25]. The high concentration of these generated gases is a concern to avoid explosive conditions since the water radiolysis under extreme conditions is not fully understood due to the rich and inherent complexity of chemical activity [26].

There is extensive experimental and theoretical rate constant investigation of the title reaction [5] and, due to its importance, many potential energy surfaces (PES) have been proposed to estimate theoretically thermodynamic and kinetic parameters. Chen et al. [27] proposed recently a global PES using neural networks method based on approximately 17,000 *ab initio* energies calculated via UCCSD(T)-F12a/AVTZ. Additionally, quantum-classical (QC) investigations reported the connection of the reactivity of H_2 with vibrational excitation energy exchange while OH radicals are not affected [28]. Recently, Kastner et al. [20] obtained theoretical reaction rate constant, in the range of the 150 K to 1000 K, with excellent agreement with experimental data. Talukdar et al. [29] and Bhattacharya et al. [6] demonstrated the presence of an isotopic effect in the reaction involving molecular hydrogen - especially in low-temperature conditions – a classical signature of quantum tunneling effect [6, 29].

Here, the H_2 + OH reaction in the gas-phase and in the aqueous environments (due relevance in living organism previously described) has been investigated with a blend of electronic structure calculations - Quadratic Configuration Interaction involving single, double and triple substitutions excitations QCISD(T), with the *deformed*

Transition-State Theory (*d*-TST) to account for the tunneling effect. A similar approach was previously developed and illustrated by our group in various cases of four-body reactions, with promising results suggesting a significant role of stereodynamics, roaming and quantum effects in influencing the rates of reactive [18, 20, 30–32], so qualifying our theoretical tools to cope with this reaction.

2 Computational Procedures

2.1 Stationary Electronic Structure Calculations

The electronic structure properties of the reactants, the products, and the transition state were calculated employing the Møller-Plesset [33], Configuration Interaction [34], in combination with 6-311++G(3df,3pd) and aug-cc-pVDZ basis set. The specific level of calculation was selected to perform analyses and comparison with experimental data: CISD(T)/aug-cc-pVDZ//MP2/6-311+G(3df,2pd). The stationary points were characterized by analytic harmonic frequency calculations. The absence or existence of one imaginary frequency for crossing the barrier characterizes the optimized structures as local minimum or transition state, respectively. The zero-point vibrational energy contributions were considered in the calculation of the barrier. To account for the solvent effect the continuum solvation model density was applied to mimicking the water ambiance (SMD) [35].

2.2 Reaction Rate Theories

The reaction rate constants (k) were calculated by deformed-transition state theory (*d*-TST). This phenomenological formulation covers cases of concave deviation from Arrhenius law against the reciprocal of temperatures for elementary chemical reactions, exhibiting *sub*-Arrhenius behavior. In general, this behavior is a signature of quantum tunneling. To account the quantum tunneling in chemical reactions in the *deformed* formulation, d parameter is introduced from transitivity concept γ [36, 37] namely the inverse of activation energy ($1/E_a$) with reciprocal of the temperature (β) truncated at an order higher than one:

$$\gamma \equiv \frac{1}{E_a} = \frac{1}{\varepsilon^{\ddagger}} \quad - d\beta \tag{1}$$

where $\varepsilon^{\ddagger}$ is a constant and represents an energetic obstacle to the reaction at high temperatures and $\beta = 1/k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature. In Ref. [38], an explicit procedure for calculation of d was developed as inversely proportional to the square of the barrier ($\varepsilon^{\ddagger}$) and directly proportional to the

square of the frequency for crossing the barrier ($v^{\ddagger}$) at maximum in the minimum energy path on the potential energy surface,

$$d = -\frac{1}{3}\left(\frac{hv^{\ddagger}}{2\varepsilon^{\ddagger}}\right)^2 \tag{2}$$

where h is Planck's constant.

The tunneling corrected averaged by Boltzmann factor from TST formulation was replaced by the deformed exponential function, yielding the d-TST formulation [39]

$$k(\beta) = \frac{1}{h\beta}\frac{Q^{\ddagger}}{Q_{Reac}}\left(1 - d\varepsilon^{\ddagger}\beta\right)^{1/d} \tag{3}$$

where Q_{Reac} and $Q^{\ddagger}$ are the partition function (translational, vibrational, rotational and electronic contributions) of the reactants and of the activated complex, respectively. Equation (4) recovers the TST rate constant when d tends to zero, due to the Euler limit, $\lim_{d\to 0}\left(1 - d\varepsilon^{\ddagger}\beta\right)^{1/d} = e^{-\varepsilon^{\ddagger}\beta}$.

The tunneling regime can be characterized considering the crossover temperature parameter $T_c = hv^{\ddagger}/2\pi k_B$[40, 41], conventionally establishing (within some arbitrariness) the ranges of the regimes for a specific imaginary frequency at the top of the barrier point, $v^{\ddagger}$: negligible ($4T_c > T > 2T_c$), moderate ($2T_c > T > T_c$) and deep ($T_c > T$) regimes.

A phenomenological representation for the temperature dependence of obtained rate constants to cover the regimes, except at deep tunneling, can be obtained by Aquilanti-Mundim deformed Arrhenius formula (AM) [42]

$$k(\beta) = A(1 - \bar{d}E_0\beta)^{1/\bar{d}} \tag{4}$$

A and $\bar{d}$ are the pre-exponential factor and the deformed parameter, respectively. [Note a change in the notation here, needed in order to avoid ambiguities: in terms of the fitted equation, we defined $\bar{d}$ which is different from d and E_0 which is different from $\varepsilon^{\ddagger}$.

All kinetic and associated parameters were calculated with the Transitivity Code-version 1.0.0: details of the computational program can be found on the www.vhcsgroup.com/transitivity web page.

3 Results and Discussion

Table 1 shows theoretical imaginary vibrational frequency (cm^{-1}), crossover temperature and relative energies (in kcal mol^{-1}) of the stationary points along the $H_2 + OH \rightarrow H_2O + H$ reaction coordinate at carefully chosen different levels of

theory. The transition state in gas-phase presents an imaginary vibrational frequency of 1531*i* at MP2/6-311++G(3df,3pd), clearly different from the result obtained by Meisner and Kastner (1199*i*) at CCSD(T)-F12/cc-pVDZ-F12. Consequently, a difference around 100 K is observed for crossover temperature. This difference suggests an improvement in our calculation, which was performed only in energy at CISD(T)/aug-cc-pVDZ//MP2/6-311+G(3df,2pd) level.

Table 1. Imaginary vibrational frequencies $(\nu^{\ddagger})$ in cm^{-1}, cross over temperature (T_c) in Kelvin, the barrier height $\left(\varepsilon^{\ddagger}\right)$ and exothermicity-type energies in $kcal.mol^{-1}$ for OH + H_2 reaction both gas- and aqueous-phase. Theoretical data are also presented for comparison.

	$\nu^{\ddagger}$	T_c	$\varepsilon^{\ddagger}$	ΔE
Gas-phase [MP2]	1531*i*	350	8.05	−22.97
Gas-phase [CISD(T)//MP2]	–		6.63	−14.30
Aqueous-phase [CISD(T)//MP2]	–		6.27	−16.71
Meisner and Kastner (Gas phase) [20]	1199*i*	270	5.38	−16.27

Table 1 also present barrier height calculated at MP2 level of theory in gas-phase, around 8 $kcal.mol^{-1}$, different from Meisner and Kastner obtained with coupled cluster level of calculation. However, our calculation yields a significant decrease in barrier energy and in exothermicity values at CISD(T)/aug-cc-pVDZ//MP2/6-311+G(3df,2pd) level with a reasonable agreement with Meisner and Kastner [20]. To account for the solvent effect, the continuum solvation model density was applied for mimicking the aqueous-phase (SMD) at CISD(T)/aug-cc-pVDZ//MP2/6-311+G(3df,2pd) level of calculation. Comparison between gas- and aqueous-phase presents a slight decrease in the barrier height at the similar level of calculation.

We calculate the kinetic rate constant using deformed-Transition State Theory (d-TST) in a realistic range of temperature (250–350 K) at CISD(T)/aug-cc-pVDZ//MP2/6-311+G(3df,2pd) level of calculation for the title reaction in gas- and aqueous-phase. Figure 1 shows the comparison of the *d*-TST rate constant with previous theoretical [20, 43] and experimental [29, 30, 44–47] results for $H_2 + OH \rightarrow + H_2O + H$ reaction: it is observed a slight difference with the literature in reaction rate constants in gas-phase, and an improvement in the reactivity with the inclusion of solvent effect. Here, we show experimental data of the reaction rate constants in aqueous-phase [48–50], and our preliminary calculations yield a reasonable qualitative agreement.

In this work, we use the AM formula, Eq. (4), to fit the temperature dependence of the reaction rate constants in gas- and aqueous-phase. AM formula has been successfully applied to a variety of chemical processes [42, 51–56]. The temperature dependence of the reaction rate constants can be expressed as

$$k_{Gas}(T) = 2.94 \times 10^{-10}\left(1 + \frac{459.40}{T}\right)^{-12.32}, \tag{5}$$

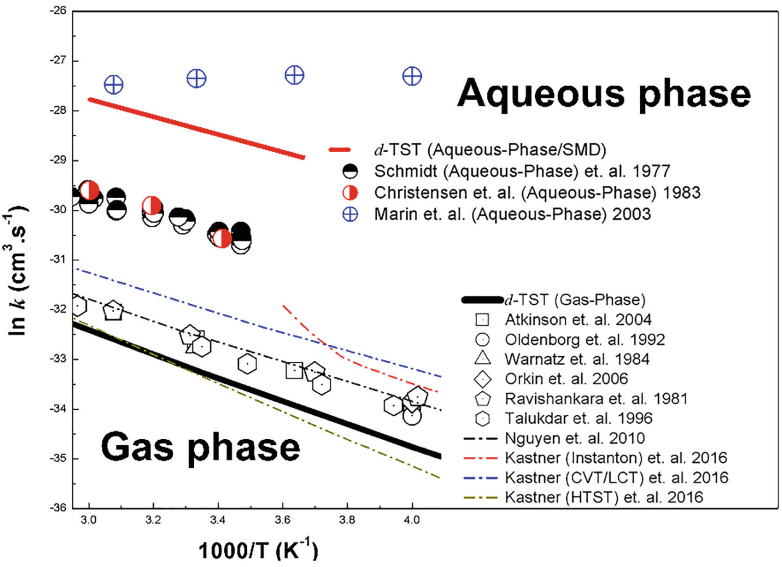

Fig. 1. Comparison of the *d*-TST rate constant with previous theoretical [20, 43] and experimental [29, 30, 44–47] results for $H_2 + OH \rightarrow + H_2O + H$ reaction.

and

$$k_{Aqueous}(T) = 1.64 \times 10^{-9}\left(1 + \frac{479.95}{T}\right)^{-8.55}. \tag{6}$$

The water environment produced a significant effect in the reactivity of the molecular hydrogen with hydroxyl radical as observed in Fig. 1. The reaction rate constants in aqueous-phase increase approximately 150- and 138-fold at 25 °C and 36.5 °C, respectively, see Eq. (7). The former temperature is conventionally used as the referential temperature in chemical reactions and the last mimics the human corporal temperature.

$$\frac{k_{Aqueous}(25\,^{\circ}\mathrm{C})}{k_{Gas}(25\,^{\circ}\mathrm{C})} \approx 150; \quad \frac{k_{Aqueous}(36.5\,^{\circ}\mathrm{C})}{k_{Gas}(36.5\,^{\circ}\mathrm{C})} \approx 138 \tag{7}$$

4 Conclusion

In summary, in this work we established the role of the aqueous environment for the OH + H_2 reaction based on high-level *deformed* Transition-State Theory. The following key findings emerged from our investigation and support the assumptions presented in this work:

- All the stationary points with the energetics and geometric parameters involved in the reaction were accurately characterized at the CISD(T)/aug-cc-pVDZ//MP2/6-311+G(3df,2pd) level of calculation.
- *Deformed* Transition-State Theory is shown to be suitable for describing the reaction rate constants in gas- and aqueous-phases.
- Water ambiance produced a significant effect in the reactivity of the molecular hydrogen with hydroxyl radical, approximately 150- and 138-fold at 25 °C and 36.5 °C, respectively.

We expect that these results will pave the way to future studies for medical and technological applications.

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