DETERMINATION OF THE RATE CONSTANT FOR THE REACTION

\[ \text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O} \] by \textit{ab initio} \text{CALCULATION}

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Abstract

Correlated \textit{ab initio} electronic structure calculations relative to the hydrogen abstraction reaction by hydroxyl radical from hydrogen-peroxide have been investigated. The results are used, with the zero-order interpolated variational transition state theory (IVTS-0), to evaluate the rate constants \( k(T) \) of the title reaction over a wide range of temperature \( T \). The calculated rate constants are in good agreement with the experimental ones and confirm the "anomalous" behavior of \( k(T) \) observed experimentally.

Keywords: \textit{ab initio}; Transition state; Tropospheric; Kinetics.

1. Introduction

The high chemical reactivity of the hydroxyl radical plays a central role in tropospheric chemistry. The OH radical is known to act in the troposphere as a detergent by its reactions with many compounds, thus the concentration of any compound in the troposphere is induced, in part, by the kinetic of its reaction with OH radical. In turn, rising in concentration of pollutants may change the concentration of OH via its loss reactions. One of the important loss OH reactions, which attract significant attention, is its reaction with hydrogen-peroxide

\[ \text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2. \] (1)

There have been numerous experimental measurements of the rate constant \( k(T) \) of reaction (1) over a wide range of temperature \( T \) [1-5]. The experimental results shows two principal aspects:

- a small temperature dependence of \( k \), and
- a strong up-turn of \( k \) at temperature near 800K.

By comparison with experimental results of \( k(T) \) for others hydrogen abstraction reactions by hydroxyl radical[6-7], the experimentalists deduce that these aspects are anomaly and they call this "anomalous behavior" of \( k(T) \). They suggests for this reaction a two step mechanism involving an \( \text{H}_2\text{O}_3 \) intermediate complex [5] to explain this "anomalous".

Our goal in this work is to test a one step mechanism hypothesis in reproducing experimental results of \( k(T) \). In our knowledge there are no yet \textit{ab initio} transition state calculation of the rate constant for the title reaction.

To reach our goal we have performed an \textit{ab initio} calculation of the structures, energies and vibrational frequencies of the reactants (\( \text{H}_2\text{O}_2,\text{OH} \)), products (\( \text{HO}_2,\text{H}_2\text{O} \)) and saddle point for reaction (1). We have used these electronic structure calculations with the zero-order interpolated variational transition state theory (IVTST-0) [8] to evaluate the rate constant \( k \) with respect to temperature variation. We compare the calculated rate constants to experimental ones in order to test the reliability of the theoretical method used in predicting the kinetics of reactions.

2. Computational method

2.1 Electronic structure calculation

All the \textit{ab initio} calculation of the equilibrium geometry and force constant matrix of the reactants, products and transition state were done with the HONDO95.3 program [9], using the Dunning’s consistent correlation polarized basis set (cc-pVTZ) [10]. Each species implied in reaction (1) is taken in its ground-state. The geometry, energy and vibrational frequencies of the reactants and products were calculated at the ROHF/MP2 level. We have optimized the transition state geometry in a CASSCF calculation with an active space including three electrons in three active orbitals : the \( \sigma_{\text{OH}}, \sigma^*_{\text{OH}} \) bond orbitals and the non-bonding \( p \) singly occupied orbital of
OH. The energy was then corrected for the remaining electron correlation in a second-order perturbation calculation with the CASSCF zeroth order wave function with the OPT2 choice (CASPT2) [11].

2.2 Rate constant calculation

Rate constants are calculated in the zero-order semi-classical interpolated transition state theory [8]. In this model information needed is only available at the reactant (R), the saddle point ( ), and product (P) and the rate constant is given by

$$ k_{TST/ZCT-0} (T) = \kappa_{ZCT-0} (T) k_{TST}(T), $$

where \( \kappa_{ZCT-0} (T) \) is a ground-state transmission coefficient which primarily accounts for tunneling correction.

In the present work the transmission coefficients is calculated in the zero-curvature ground-state tunneling (Z.C.T) method with the zero-order (-0) interpolation of the reaction path.

$$ k_{TST} (T) = \frac{\sigma Q^R(T)}{\beta h Q^T(T)} \exp(-\beta V^*), $$

is the conventional transition state theory (TST) rate constant without tunneling [12]. \( \sigma = 2 \) (for this reaction) is the symmetry factor accounting for the two symmetry-related reaction path (there are two possibilities to hydrogen abstraction from \( \text{H}_2\text{O}_2 \)). \( \beta = 1/\text{K}T \), \( \text{K} \) is the Boltzmann's constant, \( h \) is Planck's constant , \( Q^R(T) \) is the reactant partition function per unit of volume, \( V^* \) is the classical barrier height and \( Q^T(T) \) is the partition function of the transition state.

3. Results and discussions

3.1 Electronic Structure Calculations

The \textit{ab initio} calculations of the optimized geometry for reactants (\( \text{H}_2\text{O}_2,\text{OH} \)) and products (\( \text{HO}_2, \text{H}_2\text{O} \)) are a simple task and the results for calculated geometrical parameters and harmonic frequencies are in good agreement with the corresponding experimental values. The major difficulty in such study is the location of the transition state. For this reason we do not present here results relative to geometry optimization and harmonic frequency calculations for reactants and products (more information is available upon request to the author).

The geometry parameters of the transition state (TS) are collected in Fig. 1. We note that at the TS the breaking O-H bond (O1-H3) is shorter than the forming one (H3-O5) which is consistent with the fact that reaction (1) is exothermic and it occurs earlier on the reaction path. The unique imaginary frequency \( \omega^* \) corresponds to the reaction coordinate (H3 moving from O1 to O5), its CASSCF value \( \omega^* = 4480 \text{ i cm}^{-1} \) is very large and its use to calculate tunnel effect contribution to the rate constants by Wigner method [14] can lead to the results with no physical signification (it lead for this reaction to a minimum in \( k(T) \), overset which is not experimentally confirmed ). The surestimation of the \( \omega^* \) value by the CASSCF method is also detected for \( \text{C}_2\text{H}_6 + \text{OH} \) reaction compared to MP2 calculation [15].

3.2 Rate constant calculation

In Table 1 we have collected the calculated values of the TST and TST/ZCT-0 rate constants, for the temperature range from 200 to 2000K, experimental activation energy from Arrhenius fit range from 0.3 to 0.8 kcal.mol\(^{-1} \) [1-3,17,18].

Figure 1 : Geometry of the transition state (lengths in Å, angle in degrees).
together with the experimental values \( k_{\text{exp}} \). Fig. 2 shows the plot of the calculated (TST, TST/ZCT-0) and the experimental rate constants versus 1000/T, T is the temperature in Kelvin.

First we note that TST/ZCT-0 calculation predict rate constants for the title reaction of the same order of magnitude as the experimental data. The calculated values of \( k_{\text{TST/ZCT-0}}(T) \) underestimate the experimental ones by a factor ranging from 1.1 to 3. The good agreement support our \textit{ab initio} calculation.

If we consider the factor: 
\[
\frac{k_{\text{TST/ZCT-0}}(T=1000 \text{ K})}{k_{\text{TST/ZCT-0}}(T=200 \text{ K})}
\]
for the present reaction and a value about 1000 for the well studied CH\(_4 + OH \) reaction [19-21], thus our calculation confirm the small temperature dependence of the rate constant. Both TST and TST/ZCT-0 rate constants (Fig. 2) exhibit a strong up-turn at T near 800K.

<table>
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<th>T(K)</th>
<th>( k_{\text{TST}} )</th>
<th>( k_{\text{TST/ZCT-0}} )</th>
<th>( k_{\text{exp}} )</th>
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<td>( ^c )</td>
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**Table 1**: Calculated and experimental rate constants (cm\(^3\)molecule\(^{-1}\).s\(^{-1}\)).

\(^a\)Power of 10 in parentheses, \( ^b \) ref [1], \( ^c \) ref [3], \( ^c \) from fitted expression of Ref [5].

\[ k(\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}) \]

**Figure 2**: Plot of calculated and experimental rate constant \( k(\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}) \) versus 1000/T(K).
4. Conclusion

We have calculated the rate constants of hydroxyl radical abstraction reaction with hydrogen peroxide for temperature from 200 to 2000K. Our results, established with consideration of a one step mechanism does which not involve an intermediate complex forming H₃O₃ along the reaction path, is in good agreement with the experimental results and confirm the experimental observations. The present study of the tittle reaction confirm the remarkable success of the combined (ab initio- IVTST) method in predicting kinetic information for reactions even with low-barriers.

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References