

Kinetics of Ozone Decomposition in Gas and Aqueous Phases Using Quantum Chemical Reaction Calculations

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Abstract - An *ab initio* study was conducted to investigate the kinetics of the ozone degradation in gas and aqueous phases considering the reaction of ozone with hydroperoxyl radical using coupled cluster calculations (CCSD) method. Oxygen atom transfer and hydrogen atom transfer are studied and compared as two potential transition state paths. The *ab initio* quantum chemical calculations showed that the calculated overall rate constant in the gas phase differs by almost an order of magnitude from the measured values. However, the calculated selectivity (branching fraction) of hydrogen atom transfer is almost exactly the experimental value at room temperature, which was measured directly with isotope studies. This result may affect our understanding of atmospheric ozone chemistry.

Keywords: Ab Initio, Ozone Degradation, Hydroperoxyl Radical, Coupled Cluster Calculations, Quantum Chemical Calculation, Branching Fraction, Isotope.

1. Introduction

Ozone is a widely used oxidant due to its ability to destroy a wide range of pollutants [1]. There are a number of studies showing that molecular ozone reactions with species in water tend to be highly selective [2, 3]. On the other hand, reactions with the hydroxyl radical, an ozone decomposition by-product, are non-selective, leading to faster reaction rates and degradation of compounds [4-6]. The mechanism of ozone decomposition includes a chain of reactions yielding highly reactive radicals, and therefore, two types of reactions occur during ozonation: the interaction of molecules with molecular ozone and radical reactions. [7-10].

Since decomposition of ozone in aqueous solution plays a very important role in the application of ozonation processes, the mechanism of aqueous ozone decomposition has been studied for several decades [8, 10-12]. However, most studies on the decomposition of O₃ in water are primarily based on overall kinetics found for pure water and the mechanism is kinetically complex due to the production of free radicals, which may either be scavenged by bicarbonate and organic solutes or react with the remaining ozone molecules to yield more free radicals [7, 13]. Despite many studies conducted in this area, the decomposition mechanism of ozone is still not completely understood. Consequently, the existing kinetic models of ozone decomposition in aqueous phase have not been able to predict the process well in a broad range of pH [11, 14], leaving a gap in our understanding of the process. Moreover, the decay of ozone is influenced by a large number of factors, especially in the presence of other compounds, and the occurrence of small amounts of impurities [15]. Hence, the kinetics of the ozone decomposition process is not well understood and the obtained results are sometimes contradictory, deviating by 3 orders of magnitude. For instance, different reaction orders are reported for the decomposition of ozone in water at the same pH [11, 16].

The impact of ozone concentration appears to be not clear since a number of authors report various kinetics orders and when first order is assumed the half-lives are distributed over a wide range. Furthermore, several factors, including pH, concentration of organic carbon and anions/ cations, and alkalinity can potentially influence the decay constant. These effects have been explained in many discordant ways [11]. Considering the substantial variability observed, it is fairly difficult to propose a general and definite mechanism for the process, indicating that the kinetics of the ozone decomposition in aqueous solutions is not clearly understood yet.

A comparison between a chemical kinetic model based on the reactions reported in the literature and the results of the conducted experimental studies in this area, indicates a substantial deviation from experimental results. This finding suggests the existence of a number of other reactions that have not been considered in the mechanism yet. Oxygen-hydrogen chemistry studies of aqueous phase atmospheric reactions, show that the reaction $O_3 + HO_2 \rightarrow OH \cdot + 2O_2$ has the potential to solve this problem [16, 17]. In particular, in combination with the reaction $O_3 + HO \cdot \rightarrow HO_2 + O_2$, this would create a chain reaction mechanism of ozone decomposition.

Although the chemistry of the additional reaction is well investigated in the gas phase [18, 19] there is a conspicuous lack of reported kinetic data in aqueous phase. There are few studies reporting a rate constant of the reaction in water [17, 20]. Chameides and Davis [18] estimated a rate constant of $4 \times 10^6 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ for the reaction based on a 1:40 ratio for reaction rates ($O_3 + HO_2 / O_3 + OH \cdot$), and Graedel et al. [20] used this rate constant in their model for droplet chemistry. Sehested et al. [17] reported the rate constant to be as low as $10^4 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$. However, the validity of these rate constants were questioned by others. Furthermore, the reported rate constants differ by several order of magnitude. The number of assumptions made to measure the rate constant (e.g., 1:40 ratio for reaction rates) as well as the limited available data about the kinetics of this reaction and how the rate constants are obtained, cast doubt on the reliability of these rate constants. In the gas phase, a value of $2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, equivalent with $1.2 \times 10^6 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ has been found [21, 22]. The reaction of hydroperoxyl radical with ozone is known to exist in the gas phase, but most the studies conducted in the liquid phase have only considered the reaction with the dissociated peroxy radicals and this reaction has not been taken into account in any water phase study yet.

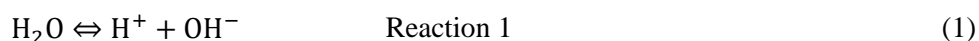
Since the kinetics of $O_3 + HO_2 \rightarrow OH \cdot + 2O_2$ in the aqueous phase has not been comprehensively studied thus far, the rate constant needs to be calculated in order to consider this reaction in the kinetic model and explore the influence of this reaction on the overall ozone decomposition kinetics. However, it is difficult to measure the rate constant in the aqueous phase through experimental procedures, because of the many interfering reactions. Quantum chemical reaction calculations are powerful tools to calculate the optimized geometries for reactants and products, locate intermediates and transition states, and obtain reaction kinetics for different reaction pathways with a reasonable accuracy to examine how the path and orientation of approaching reactants lead to a chemical reaction [23, 24]. To fill the knowledge gap, the purpose of this study is to calculate the rate constant of the $O_3 + HO_2 \rightarrow OH \cdot + 2O_2$ reaction in the aqueous medium using the Gaussian 09W package and GaussView 5 molecular modelling software [25].

The reaction with the obtained rate constant was included in a detailed model of ozone degradation in water including a total of 24 reactions. The current study can help better understand the reaction of ozone in water, provide solutions to minimize the deviation of rate constant between simulation and experimental studies, and is an opportunity to compare the rate constants in the gas and aqueous phases. Understanding the mechanism of ozonation in aqueous phase could also broaden our knowledge of ozone chemistry and pollutant degradation in aerosols, and hence of photochemistry in the atmosphere [26-28].

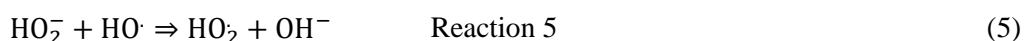
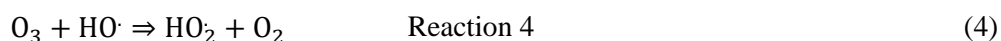
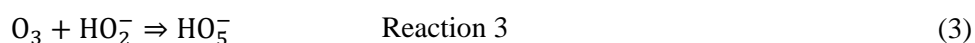
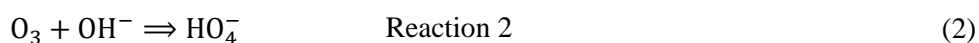
2. Chemical Kinetic Model

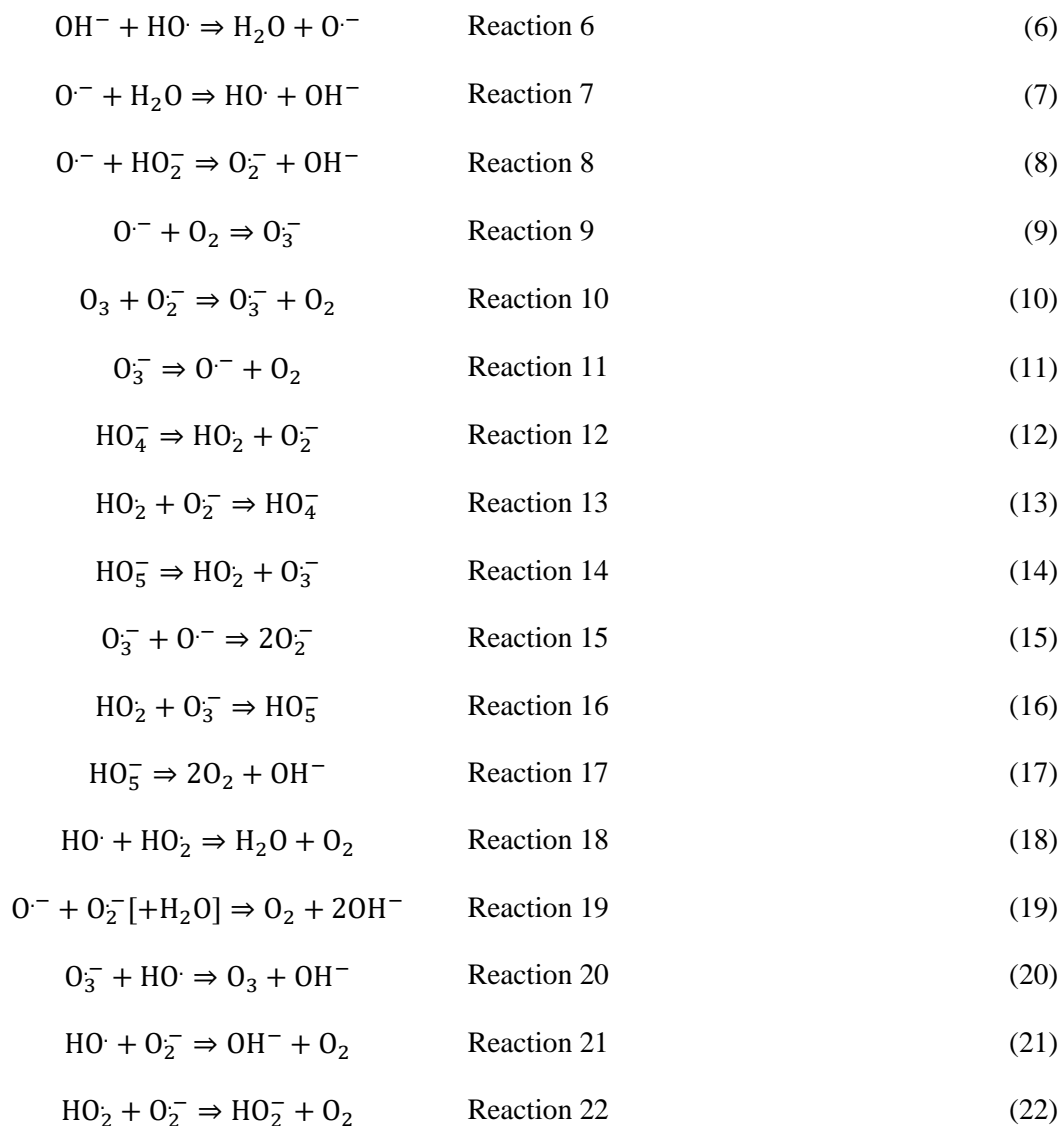
A plausible mechanism was developed based on the available ozone decomposition literature in the water phase [8, 9, 11, 29]. The following reactions are considered in the model:

Equilibrium:



Kinetics:





It is assumed that the aqueous system is without buffer solution and the reactions of different species with buffer ions are ignored. The rate constant of the reactions 2 to 22 are summarized in Table 1.

Table 1: Rate (k_i) and equilibrium constants (K_i) of the reactions participating in decomposition process of ozone in water.

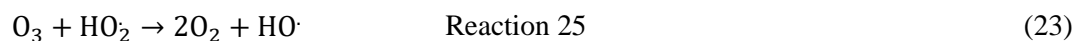
Constant	Value	Unit	Reference
K_1	10^{-14}	–	
k_2	175	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_3	2.8×10^6	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_4	2.0×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[30]
k_5	5.6×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[31]
k_6	1.2×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[32]
k_7	9.6×10^7	s^{-1}	[11]
k_8	1.0×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[9]
k_9	3.5×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{10}	1.5×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[8]
k_{11}	1.9×10^3	s^{-1}	[11]
k_{12}	10^7	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{13}	5.0×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{14}	10^7	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{15}	7.0×10^8	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[29]
k_{16}	5.0×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{17}	10^7	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{18}	6.6×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[29]
k_{19}	6.0×10^8	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[29]
k_{20}	2.5×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]
k_{21}	5.0×10^9	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[29]
k_{22}	10^8	$m^3 \cdot kmol^{-1} \cdot s^{-1}$	[11]

Based on the chosen kinetics scheme, a system of differential equations, describing the time dependence of the concentrations of different species involved in the ozone decomposition process was composed. Solving the system of differential equations provides us with apparent rate constant for ozone decomposition. The differential equations were solved with Gear's algorithm as implemented in MATLAB R2015b.

3. Computational Methods

3.1. Optimization of Reactants and Products

The reaction between ozone and HO_2 (Reaction 25) was evaluated by using the Gaussian 09 molecular modelling package. The molecular structures were plotted by the GaussView software.



Based on the literature [33-35], CCSD(T)/6-311++G(3df,spd), CCSD/aug-cc-pvdz, QCISD/6-311++(d,p), and QCISD/6-311++(d) are the commonly used methods and basis sets to optimize the structure of ozone. Although the reaction occurs in aqueous phase, no experimental data has been reported for the ozone structures in the aqueous phase. Therefore, to explore which level of theory is more suitable for the optimization of the reaction, the optimization of ozone in the gas phase was performed as well. The most suitable method and basis set were determined through comparison of ozone bond lengths and angles of calculated stable structures with the corresponding values of the experimental data [36]. The results of the optimization are shown in Table 2. Comparing the calculated results (117.2° ; $1,259 \text{ \AA}$) with the experimental data in gas phase (116.8° ; 1.278 \AA), [36] it was found that the bond length and bond angle when using the CCSD/aug-cc-pvdz level of

theory is the closest to the experimental data; therefore, CCSD/aug-cc-pvdz was chosen for optimizing other species of the reaction.

Table 3 compares the calculated bond lengths and angles of reactant and products with the corresponding experimental values in gas phase [36]. As this table represents, the calculated values are within the range (maximum 3.2% deviation) and are mainly larger than the experimental values. Therefore, the chosen level of theory is accurate enough and can be used for optimization in the aqueous phase. The stable structures of reactants and products in the gas and aqueous phases using CCSD/aug-cc-pvdz level of theory are in the supplementary information.

Table 2: Calculated and experimental bond characteristics and thermodynamics of optimized ozone under different level of theory in gas phase.

Level of theory	Bond length (Å)	Bond angle (degrees)
CCSD(T)/6-311++G(3df,3pd)	1.320	109.500
CCSD/aug-cc-pvdz	1.259	117.230
QCISD 6-311++(d,p)	1.255	117.935
QCISD 6-311+(d)	1.255	117.935
Experimental data	1.278	116.8

Table 3: Calculated (CCSD/aug-cc-pvdz) and experimental bond lengths and angles of different species in gas phase.

Species	Bond	Bond Length (Å)		Angle (degrees)	
		Experimental	Calculated	Experimental	Calculated
O₃	O - O	1.278	1.259	116.80	117.23
HO₂	O - O	1.333	1.357	104.29	105.57
	O - H	0.971	1.002		
O₂	O - O	1.207	1.198	-	-
HO·	O - H	0.970	0.991	-	-

3.2. The Transition State (TS) and Relative Energies

After optimization of the reactants and products, the transition state was calculated by the quasi-Newton synchronous transit (QST3) method and confirmed by the occurrence of a single imaginary frequency through frequency analyses. The relative energy and rate constants were calculated at 298.15 K, and 1 atm. There are two possible reaction paths for the transition state: oxygen atom transfer ($\text{HO}-\text{O}\dots\text{O}-\text{O}_2$) and hydrogen atom transfer ($\text{O}_2-\text{O}\dots\text{H}-\text{O}_2$). In this study both paths are considered and the results are compared with the experimental values. These two paths for the transition state are considered as parallel reactions, happening simultaneously.

3.2.1. Oxygen Atom Transfer

Figure 1 shows the structure of the transition state for the oxygen atom transfer in gas phase. It is shown in Figure 1 that the two O–O bond lengths in the ozone molecule are 1.33Å and 1.21Å, whereas the calculated gas phase O–O bond length in Table 3 is around 1.26Å. For the oxygen atom reaction pathway, one of the O–O bonds in ozone breaks down and another one becomes a double bond to create an oxygen molecule, therefore, the length of the one bond is expected to be longer and another one shorter than O–O bond in ozone. As Figure 1 shows, the O–O bond length in HO_2 is larger than the normal O–O bond length in this radical (1.33Å), showing that the O(5)–O(6) bond is being weakened. The H–O bond length remains almost constant as this bond will not change. The relatively long distance between O(2) and O(5) represents that these two oxygen atoms are approaching each other to create an oxygen molecule.

The results indicates that the energy of the transition state is higher than energy levels of reactants and products. Since some original bonds are weakened and the new bonds have not been completely formed yet, the transition complex is not stable. The formation of new bonds makes the transition state more stable which leads to the products. Comparing the relative energies in gas phase with the values in aqueous phase shows that the relative energy of the transition state in gas phase is

higher. Hence in aqueous phase, the reactants need to overcome a smaller energy barrier to reach the transition state, and thus, reaction is faster.

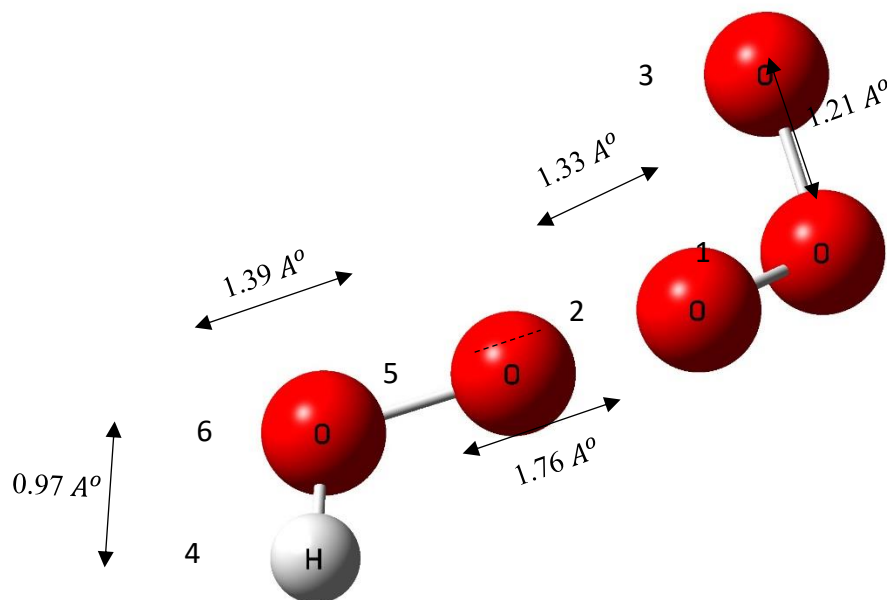


Fig.1: Structure of transition state for the oxygen atom transfer reaction pathway in gas phase (COLORED).

3.2.2. Hydrogen Atom Transfer

Figure 3 represents the structure of the transition state (hydrogen atom transfer) in gas phase. For the hydrogen atom transfer reaction pathway, the O–H bond in hydroperoxyl radical breaks down and the O–O bond becomes a double bond to create an oxygen molecule, therefore, the length of the O–H bond in the transition state is expected to be longer than O–H bond in hydroxyl radical. Figure 3 expresses the length of O–H bond is 1.37Å. Comparing this value to the calculated gas phase O–H bond length in Table 3 (~0.99Å), indicates that the O–H bond length in the transition state is longer than O–H bond length in hydroxyl radical. The relatively long distance between H(4) and O(2) represents that these two atoms are approaching each other to create an oxygen molecule.

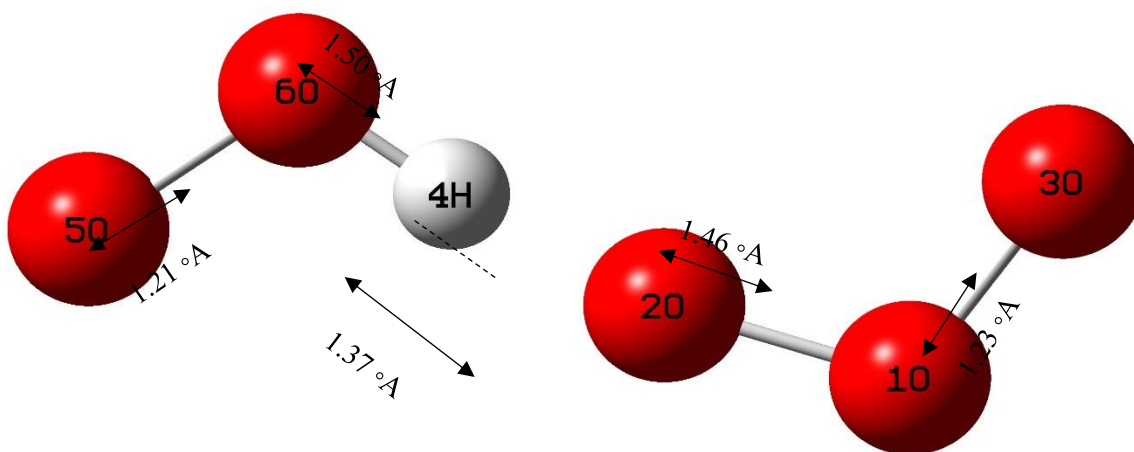


Fig. 3: Structure of transition state for the hydrogen atom transfer reaction in gas phase (COLORED).

4. Results

4.1. Reaction Rate Constants

The main reaction pathway can be expressed as:



Table 5 shows the rate constant of Reaction 25 in gas and liquid phases considering oxygen and hydrogen atom transfer in the transition state [17, 20-22]. Since both parallel paths happen simultaneously, the overall rate constant is the sum of the constants of each path.

Table 4: Experimental and calculated rate constants of the reaction between ozone and hydroperoxyl radical in gas and aqueous phases (T = 298 K).

Phase	k ($\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$) O atom transfer	k ($\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$) H atom transfer	k ($\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$) Overall	k ($\text{m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$) Experimental
Gaseous	1.0×10^4	1.3×10^5	1.4×10^5	1.2×10^6
Aqueous	3.7×10^5	8.8×10^4	4.6×10^5	10^4 to 7.5×10^6

As Table 4 represents, the calculated rate constants for the reaction in aqueous and gas phase change considerably by changing the transition state path. Comparing the obtained results implies that the H atom transfer is faster in gas phase; whereas, in aqueous phase O atom transfer is rapid in comparison with hydrogen transfer. Consequently, the overall rate constant is more influenced by O atom transfer in water. The calculated overall rate constant in the gas phase differs by almost an order of magnitude from the measured value. However, the calculated selectivity (branching fraction) of H atom transfer is 93%, almost exactly the experimental value at room temperature (92%)[21], which was measured directly with isotope studies. As mentioned before, estimations of the overall rate constant are indirect and in the presence of many competing reactions. Hence, the accurate branching ratio prediction indicates that our calculated values are accurate. The overall rate constant in the aqueous phase calculated here is within the range of experimental estimations.

5. Conclusions

This paper presented a theoretical approach for filling the gap of the mechanism of aqueous ozone decomposition at low pH by developing a chemical kinetic model, and adding a chemical reaction with a rate constant determined using quantum chemical reaction calculations. Values of 1.4×10^5 and $4.6 \times 10^5 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ were found in gas and aqueous phases, respectively for the rate constant of $\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} \cdot + 2\text{O}_2$. The calculated rate constant in aqueous phase is used in the kinetic model.

Acknowledgements

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