

A Theoretical Study on the Mechanism and Thermodynamics of Ozone-Water Gas Phase Reaction

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Ozone water reaction including a complex was studied at the MP2/6-311++G(d,p) and CCSD/6-311++G(2df,2p)/MP2/6-311++G(d,p) levels of theory. The interaction between water oxygen and central oxygen of ozone produces stable H₂O-O₃ complex with no barrier. With decomposition of this complex through H-abstraction by O₃ and O-abstraction by H₂O, three possible product channels were found. Intrinsic reaction coordinate, topological analyses of atom in molecule, and vibrational frequency calculation have been used to confirm the preferred mechanism. Thermodynamic data at T = 298.15 K and atmospheric pressure have been calculated. The results show that the production of hydrogen peroxide is the main reaction channel with $\Delta G = -21.112 \text{ kJ mol}^{-1}$.

Keywords: Complex, Transition state, Optimization, Atom in molecule

INTRODUCTION

Ozone as a reactive species plays an important role in the upper atmosphere. In view of the relatively large ozone concentration in the middle atmosphere and the importance of ozone chemistry in the depletion of ozone layer by a series of reactions with atmospheric species, its gas phase reactions are of interest. Recently, the reaction of ozone with atmospheric molecules and radicals has been studied extensively in theory and experiment [1-6].

The troposphere contains the atmospheric water vapor, though in very small concentrations (1-4%). These trace constituents play a vital role for life. A slow gas-phase reaction of ozone with water may be significant if the reaction proceeds to produce hydrogen peroxide (H₂O₂) and hydrogen tetroxide (HTO) (H₂O₄), that may be an important source of

hydroxyl radical (OH) and hydroperoxyl radical (HOO), which are well known as oxidizing agents and take part in the processes of destruction of ozone. The ozone-water complex is one of the key complexes in the reaction of ozone layer. Microwave spectra of the O₃-H₂O (1:1 complex) in the gas-phase was observed by a pulsed-beam Fabry-Perot cavity Fourier transform microwave spectrometer [7]. A few *ab initio* calculations were carried out for the H₂O-O₃ complex [8-12]. The conformer of H₂O-O₃ complex that has C_s symmetry in which the central oxygen atom of ozone and the oxygen atom of water lying on the symmetry plane was achieved as the stable configuration at the CCSD(T)/6-311++G(d,p) level of theory [12]. In this conformer, each moiety of O₃ and H₂O remains in the C_{2v} symmetry. The equilibrium ozone-water complex concentration was derived to be 2.0 ppt, which means that 0.004% of ozone may exist as the water complex [12].

In this work, we have investigated the mechanism of the reaction of O₃ with H₂O in gas-phase by isomerization and

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decomposition of H₂O-O₃ complex. We suggest three product channels with mapping the potential energy surface at the MP2/6-311++G(d,p) level of theory and predict the potential energy surface at the CCSD/6-311++G(2df,2p)//MP2/6-311++G(d,p).

Computational Methods

Geometries of the reactants, complexes, products and transition states were optimized at the spin unrestricted MP2 with the 6-311++G(d,p) bases set using the G03 program. [13]. In addition, single-point energy calculations at the CCSD/6-311++G(2df,2p)//MP2/6-311++G(d,p) were performed to predict the potential energy surface. Stationary structures, zero point energy and thermodynamic parameters were characterized by calculation of harmonic vibrational frequencies. Transition state structures were obtained from QST2 with converting reactant to product. Additionally, intrinsic reaction coordinate (IRC) calculation was performed to examine the correspondence of the calculated TS to the reactants and products. Within the scope of this method, it is possible to generate a wave function in a form suitable to execute the topological analysis atoms in molecules [14] using the AIM2000 series programs [15]. Moreover, thermodynamic data have been calculated using the statistical theory.

Atom in Molecule Theory

Several excellent reviews have been published on the theory of atoms in molecules (AIM) developed by Bader [16-17]; therefore, only a brief description of selected topological parameters relevant to the present work is presented here. This theory is based on the critical points (CP) of the molecular electronic charge density ($\rho(r)$). These are points where the electronic density Laplacian ($\nabla^2\rho(r)$) vanishes and which are characterized by the three eigenvalues of the Hessian matrix of $\rho(r)$. The CP's are labeled (r, s) according to their rank, r, (number of non-zero eigenvalues of Hessian matrix) and signature s (the algebraic sum of the signs of the eigenvalues). A positive eigenvalue indicates that the function is a minimum in the direction defined by eigenvector, and a negative sign indicates the opposite. There are four types of critical points in the electron density of molecular system: nuclear (3, -3), bond (3, -1), ring (3, +1) and cage (3, +3). Bond critical point (BCP) corresponds to a maximum in $\rho(r)$ characterized by ($\nabla^2\rho < 0$)

occurs between two neighboring nuclei, indicating the existence of a bond between them. There exists bond critical point for weak interactions. But the electron density at bond critical point is less than covalent bond and the sign of $\nabla^2\rho$ is positive.

RESULT AND DISCUSSION

The optimized geometries of reactants, complexes, transition states (TS) and products with the corresponding available experimental data, or other theoretical data [11,12] for some species, are represented in Fig. 1. The results of geometry optimization for H₂O, O₃, H₂O₂, HO₂ and ³O₂, that were obtained at the MP2/6-311++G(d,p) level of theory in this work, are in agreement with experimental values.

The complex, H₂O-O₃ (C1), is formed when the reactants approach each other. In this complex, the intermolecular bond was formed between the central oxygen atom of O₃ and oxygen atom of H₂O. Molecular geometry indicated that this complex has C_s symmetry in which oxygen of water and the central oxygen of ozone lie in the symmetry plane. This plane bisects the O-O-O angle of ozone and H-O-H angle of water. This structure of the H₂O-O₃ complex is similar to optimized structure with eclipsed form that is calculated by Tachikawa and Abe [11] and stable "double-decker" conformer, optimized at the CCSD(T)/6-311++G(d,p) [12]. Tachikawa and Abe calculated the oxygen-oxygen distance equals to 2.8552 Å at the QCISD/6-311++G(d,p) level of theory which is close to 2.874 Å at the MP2/6-311++G(d,p) level in this work. Other calculated geometrical parameters of C1 (Fig. 1) are in acceptable agreement with the results of references 11 and 12. To identify this interaction, we have used the topological analysis of charge density. The values of bond critical points parameters and electronic density gradient satisfy criteria for some important bonds such as, hydrogen bonds and weak interactions between oxygen-oxygen atoms of the candidate molecules which are schematized in Fig. 2.

The large value of electronic density gradient ($\rho(r)$) indicates strong interaction, and the positive value of electronic density Laplacian ($\nabla^2(\rho)$) shows non-covalent interaction between corresponding atoms.

The low value of Laplacian and the positive value of Laplacian from AIM analysis for C1 show that there is a weak

A Theoretical Study on the Mechanism and Thermodynamics

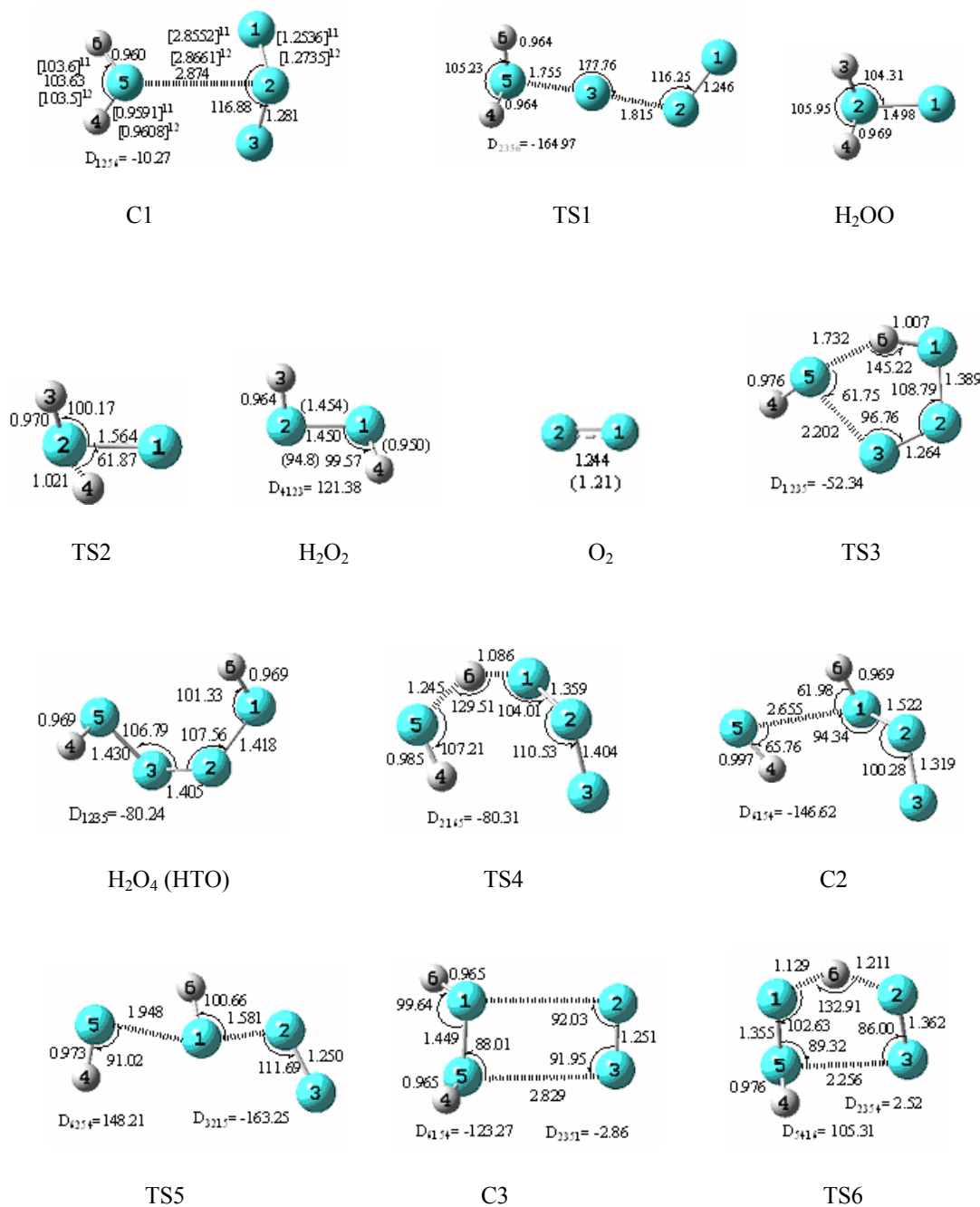


Fig. 1. Optimized geometries of reactants, products, complexes and transition states of studied reaction in the MP2/6-311++G(d,p) level of theory. Bond lengths, bond angles and dihedral angles are in Å and degree, respectively. For C1, H₂O₂, HO₂, HO₃, OH, O₂, H₂O and O₃, the experimental values are given in parentheses and bracket values refer to references [11,12,18].

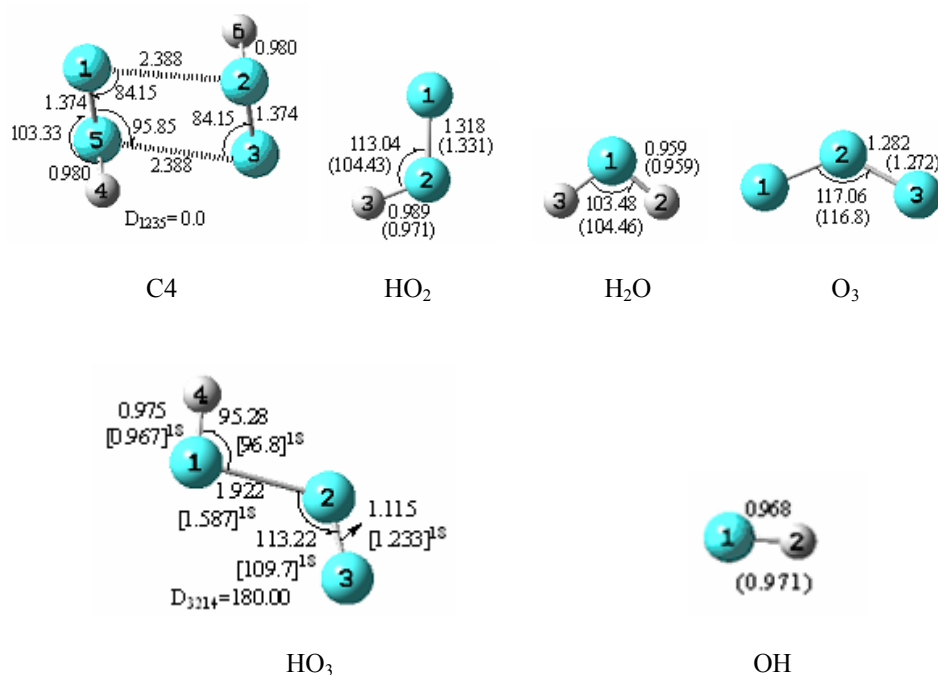


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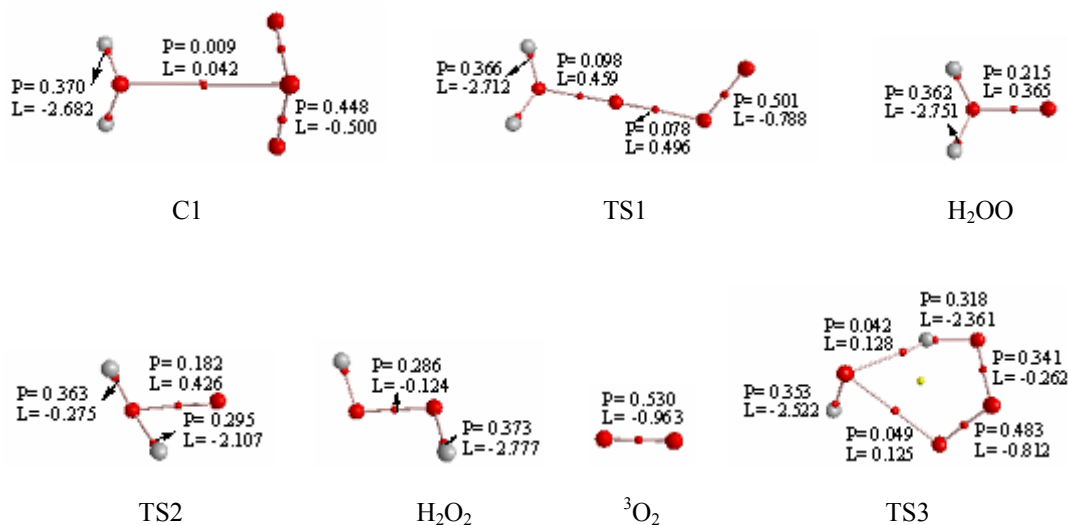


Fig. 2. The values of the AIM theory topological parameters for hydrogen and van der Waals bonds and selected covalent bonds of complexes, transition states and the other species. P and L means electronic charge density, $\rho(r)$, and electronic density Laplacian, $\nabla^2\rho(r)$, respectively.

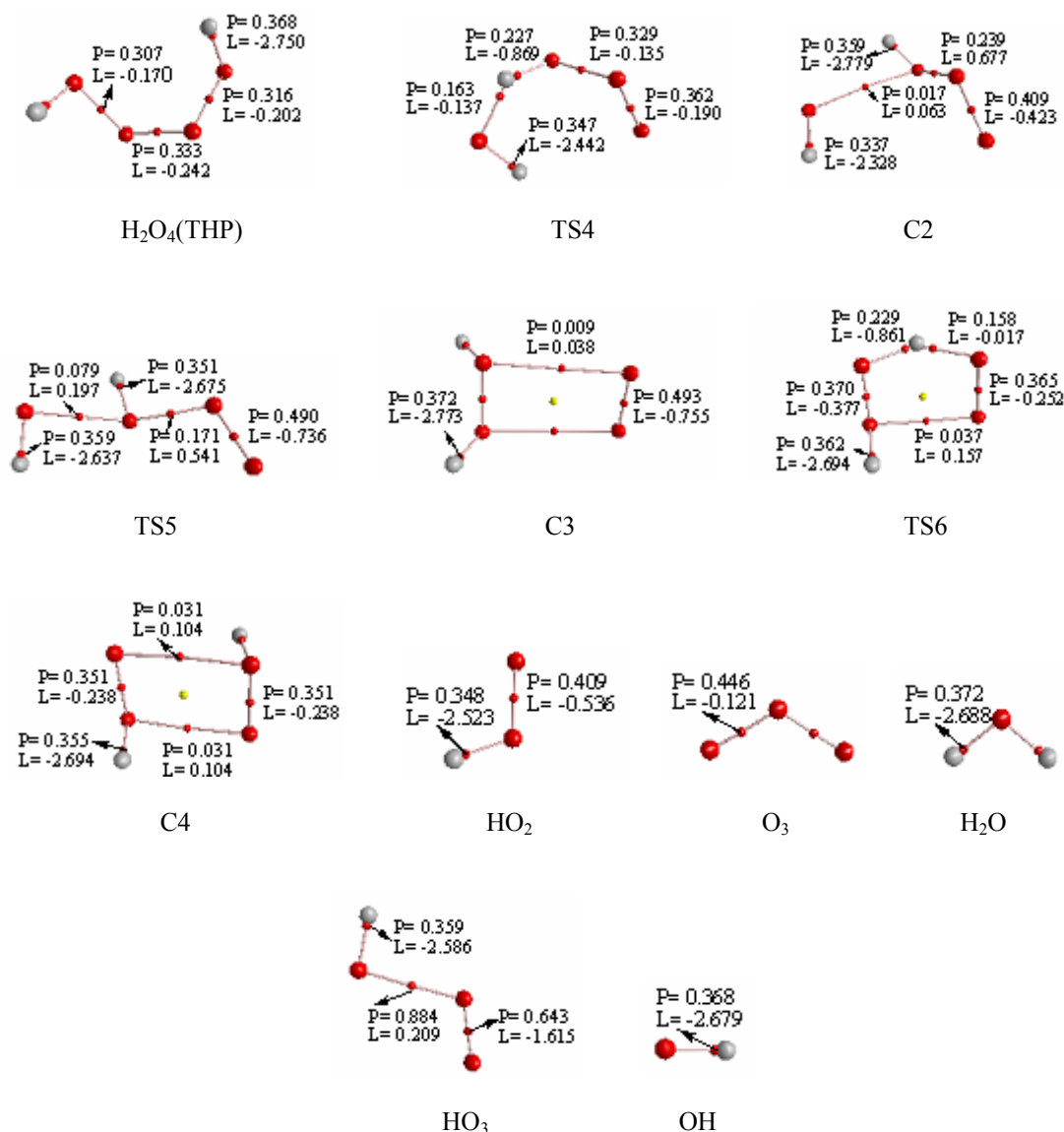


Fig. 2. Continued.

interaction (complexation) between oxygen atom of water and central oxygen atom of ozone [$\rho(r) = 0.009$ au, and $\nabla^2(\rho) = 0.042$ au]. The binding energies of C1 was calculated to be 11.098 kJ mol⁻¹. Calculation of Tsuge and *et al.* using the QCISD(T)/6-311++G(3df,3pd)//QCISD/6-311++G(d,p) level of theory indicates that the binding energy of the C1 conformer is 7.77 kJ mol⁻¹ [12]. Regarding the formation of ozone-water complex (C1), we have found six transition states (TS1, TS2, TS3, TS4, TS5, TS6) and three other stationary

points (C2, C3, C4), related to transition states TS4, TS5 and TS6, respectively. As a matter of fact, the corresponding molecular graph (Fig. 2) shows the existence of a BCP between bonded atoms.

The total energies and relative energies of reactants, complexes, transition states and products computed at the MP2/6-311++G(d,p), under atmospheric pressure and 298.15 K are listed in Table 1. Also the results of the single point energy calculations at the CCSD/6-311++G(2df,2p)//MP2/6-

Table 1. Total Energies and Relative Energies Including Zero-Point Energy Corrections for Various Species at the MP2/6-311++G(d, p) and CCSD/6-311++G(2df,2p)//MP2/6-311++G(d,p) Level of Theory. The Parentheses Values Refer to Ref. [1]

Species	MP2/6-311++G(d,p)		CCSD/6-311++G(2df,2p)//MP2/6-311++G(d,p)	
	Total energy (au)	Relative energy (kJ mol ⁻¹)	Total energy (au)	Relative energy (kJ mol ⁻¹)
H ₂ O + O ₃	-301.235	0.0	-301.363	0.0
C1	-301.240 (-301.4764) [1]	-11.098	-301.365	-5.515
C2	-301.209	69.743	-	-
C3	-301.198	98.806	-301.351	31.408
C4	-301.199	94.622	-301.325	186.670
TS1	-301.100	354.972	-	-
TS2 + O ₂	-301.152	217.755	-301.239	325.013
TS3	-301.156	207.305	-301.292	187.084
TS4	-301.176	156.412	-301.256	281.194
TS5	-301.115	315.394	-301.254	285.201
TS6	-301.173	162.051	-301.298	169.198
H ₂ OO + ³ O ₂	-301.160	196.337	-301.328	91.196
H ₂ O ₂ + ³ O ₂	-301.243	-18.972	-301.403	-105.464
H ₂ O ₄ (HTO)	-301.188	122.254	-301.358	13.418
2HO ₂	-301.155 (-301.4532) [1]	210.432	-301.340	59.564
HO ₃ + OH	-301.145	235.933	-301.294	179.634

311++G(d,p) level of theory are summarized in Table 1. The potential energy surface according to the relative energies at the MP2/6-311++G (d,p) level is shown in Fig. 3.

The vibrational frequencies of all stationary points and the vibrational mode assignment for essential frequencies of C1 at the MP2/6-311++G (d,p) level, along with the available experimental values or other calculated data [11,12] are listed in Tables 2 and 3. As can be seen, the calculated frequencies are in good agreement with available experimental or other calculated values. Obtained vibrational frequency of H₂O, O₃ and C1 complex are compared with other calculated or experimental values in Tables 2 and 3, that shows a good agreement with other results. The comparison of vibrational frequencies of free H₂O and O₃ with corresponding frequencies in C1 shows small shifts (3-14 cm⁻¹), indicating that molecular interactions are weak. The extents of red or

blue shifts of H₂O and O₃ frequencies in C1 are summarized in Table 2.

The number of imaginary frequencies (0, 1) indicates whether a minimum or transition state has been located. All the reactants, products and complexes have only real frequencies, while TS is identified with one and only one negative eigenvalue of the Hessian matrix.

For the reaction of H₂O + O₃, the stable complex (C1) can be formed; then a series of isomerization and dissociation of it can occur after passing some transition states to form the corresponding products. Three product channels have been shown in Scheme 1.

Reaction Pathway Properties

For the reaction of H₂O + O₃ both O-abstraction by H₂O from O₃ (R1) and H-abstraction by O₃ from H₂O (R2 and R3),

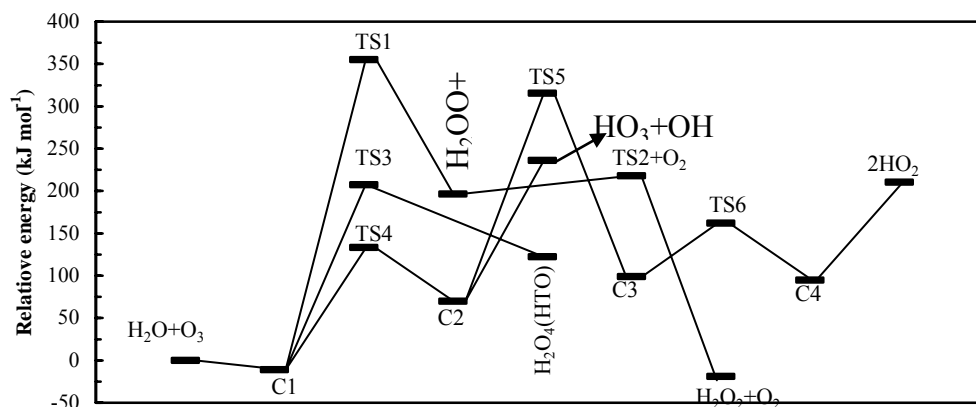


Fig. 3. The IRC curves for all the transition states that were calculated at MP2/6-11++G(d,p).

Table 2. Vibrational Frequencies, Mode Assignment and the Extent of Red or Blue Shifts of H₂O and O₃ Frequencies in C1 at MP2/6-311++G(d,p) Level of Theory

Approximate mode	C1		H ₂ O	O ₃
	Freq.	Shifts		
Inter molecular	69(51) ^a (69) ^b			
"	94(78) ^a (90) ^b			
"	95(93) ^a (93) ^b			
"	136(135) ^a (132) ^b			
"	170(153) ^a (166) ^b			
"	233(200) ^a (214) ^b			
Bending O-O-O	754(755) ^a (723) ^b	4b		750(749) ^a (723) ^b (753) ^c (767) ^g [716] ^d
Symmetric stretching O-O	1167(951) ^a (1034) ^b	3b		1164(935) ^a (1034) ^b (1006) ^c (1290) ^g [1089] ^d
Asymmetric stretching O-O	2284(1666) ^a (1657) ^b	9r		2293(1241) ^a (1152) ^b (1261) ^c (1325) ^g [1135] ^d
Bending H-O-H	1641(1251) ^a (1152) ^b	14b	1627(1654) ^a (1657) ^b (1656) ^d [1595] ^d	
Symmetric stretching O-H	3878(3897) ^a (3860) ^b	8r	3886(3889) ^a (3860) ^b (3901) ^g [3657] ^d	
Asymmetric stretching O-H	3995(3986) ^a (3962) ^b	10r	4005(3992) ^a (3962) ^b (4004) ^g [3756] ^d	

(a) Refers to reference [11], (b) refers to reference [12], (c) refers to reference [1] and (d) refers to experimental values.

Table 3. Vibrational Frequencies of all Species at MP2/6-311++G(d,p) Level of Theory

Species	Frequency (cm ⁻¹)
C2	89, 211, 273, 438, 502, 551, 638, 986, 1467, 2499, 3723, 4115
C3	52, 68, 82, 88, 108, 391, 920, 1239, 1296, 1460, 3844, 3845
C4	103, 170, 300, 383, 545, 575, 917, 1346, 1371, 1629, 3627, 3641
TS1	604i, 50, 138, 151, 348, 430, 634, 704, 1205, 1613, 3820, 3943
TS2	1291i, 802, 1012, 1415, 3177, 3797
TS3	315i, 229, 282, 433, 658, 699, 768, 907, 1447, 1620, 3112, 3706
TS4	1689i, 122, 277, 382, 589, 635, 918, 983, 1297, 1928, 3486, 4277
TS5	1347i, 172, 184, 240, 348, 493, 580, 797, 1100, 1461, 3753, 3770
TS6	1650i, 231, 317, 468, 534, 572, 960, 1149, 1322, 1444, 1791, 3682
H ₂ O ₄ (HTO)	176, 365, 396, 511, 633, 706, 869, 913, 1374, 1409, 3777, 3789
HO ₃	62, 172, 417, 837, 1989, 3726
HO ₂	1198 [1098] ^d (1135) ^c , 1429 [1392] ^d (1467) ^c , 3492 [3436] ^d (3715) ^c
H ₂ OO	784, 950, 977, 1596, 3741, 3849
H ₂ O ₂	394 [317] ^d , 920 [864] ^d , 1300 [1266] ^d , 1456 [1394] ^d , 3848 [3607] ^d , 3849 [3608] ^d
O ₂	1456 [1622] ^d

(c) Refers to reference [1] and (d) refers to experimental values.

are two possible reaction channels.

O-ABSTRACTION REACTION CHANNEL

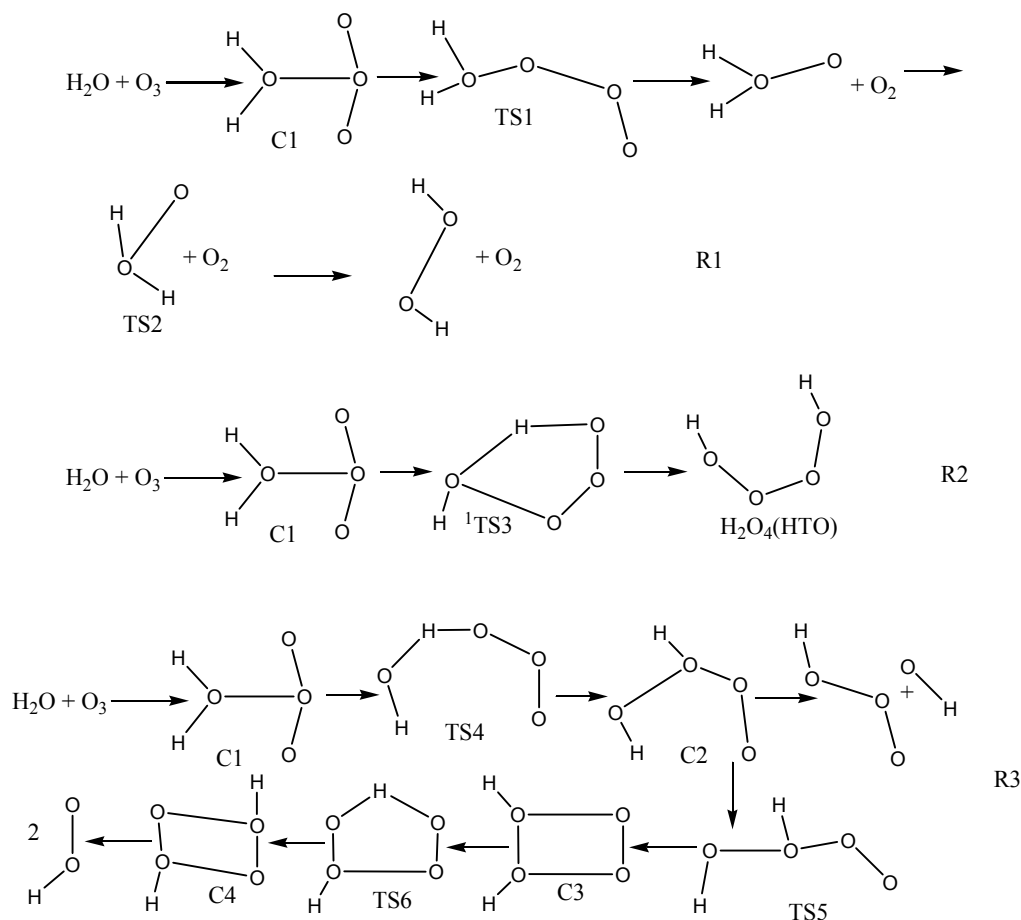
Based on our calculations, one channel (R1) for O-abstraction process has been confirmed. Reaction R1 is O-abstraction reaction to produce H₂OO and ³O₂ via C1 and TS1. The corresponding molecular graph of TS1 in Fig. 2 shows the existence of BCP between the oxygen atom of water and terminal oxygen atom of ozone [$\rho(r) = 0.098$ au and $\nabla^2(\rho) = 0.459$ au] with an O3-O5 distance of 1.755 Å. The length of the breaking O2-O3 bond at TS1 is predicted to be 1.815 Å. Also the imaginary frequency of TS1 at 604.48i cm⁻¹ denotes the cleavage of O2-O3 bond and the formation of O3-O5 bond. For producing H₂OO and ³O₂ as products from C1, IRC curve is shown in Fig. 4. All these results show that the reaction is going to produce the corresponding products (H₂OO + ³O₂). H₂OO, as the product of this channel, is metastable, so it can be converted to H₂O₂ by H-transfer process with 21.422 kJ mol⁻¹ as forward barrier of energy. The

length of breaking O-H bond in corresponding transition state (TS2) is predicted to be 1.021 Å. The final products of H₂O + O₃ reaction in this channel should be H₂O₂ + ³O₂ as observed experimentally [18].

H-ABSTRACTION REACTION CHANNELS

Two-product channels are confirmed in the H₂O + O₃ reaction based on H-abstraction process. Channel R2 is the hydrogen transfer process from H₂O to O₃ to produce new structure with H₂O₄ formula. This process begins with the formation of pre-reactive hydrogen bonded complex C1. For the reaction path taking place through TS3, IRC calculation in the forward direction yielded hydrogen tetroxide with H₂O₄ formula (Fig. 1). The resulting transition state TS3 has a five-member ring structure, where the hydrogen is transferred between O5 and O1. Also, an interaction between O3 and O5 was identified in the ring structure by the AIM topological analysis [$\rho(r) = 0.049$ au, and $\nabla^2(\rho) = 0.125$ au]. At TS3, we

A Theoretical Study on the Mechanism and Thermodynamics



Scheme 1. Three product channels of ozone water reaction

see that the bond between O5 and H6 is weakening, as the value for $\rho(r)$ decreases to 0.042 au from the C1 value of 0.370 au.

The second path for H-abstraction (channel R3) contains three complexes C2, C3 and C4 and three transition states TS4, TS5 and TS6. The imaginary frequency of TS4 (1688.69i) corresponds to the mode for proton transfer. IRC calculations in the forward and reverse directions from TS4 yielded the corresponding reactant (C1) and product (C2) (Fig. 4). The molecular structure of TS4 and C2 is displayed in Fig. 1. It can be seen that the bond between the oxygen and hydrogen atoms in H₂O has been weakened in TS4 [$\rho(r)$ = 0.163 au] and absolutely broken with no bonding interaction at all in C2. The topology analysis of AIM indicated the existence of O1-O5 intermolecular bond in C2 [$\rho(r)$ = 0.017

au]. C2 is converted to another complex named C3, which is the complex of H₂O₂ and O₂, via TS5 with 1347.54i cm⁻¹ imaginary frequency corresponding to O1-O2 dissociation as the second transition state in this path. We can see the interaction between O1-O5 in TS5 [$\rho(r)$ = 0.079 au] which is stronger than the corresponding bond in C2 [$\rho(r)$ = 0.017 au] and weaker than that in C3 [$\rho(r)$ = 0.372 au]. C3 can produce HO₂ radical through path TS6 and C4. The third transition state in this path (TS6) which has a five-member ring structure (Fig. 1) involves other H-transfer in which H6 is drawn from O1 to O2 with 1650.10i cm⁻¹ imaginary frequency, and then C4, the complex of two HO₂ radical, is formed. This stationary point has a four-member ring structure with weak interaction between O1-O2 and corresponding O3-O5 [$\rho(r)$ = 0.031 au]. So the final product should be two hydroperoxyl radicals. All

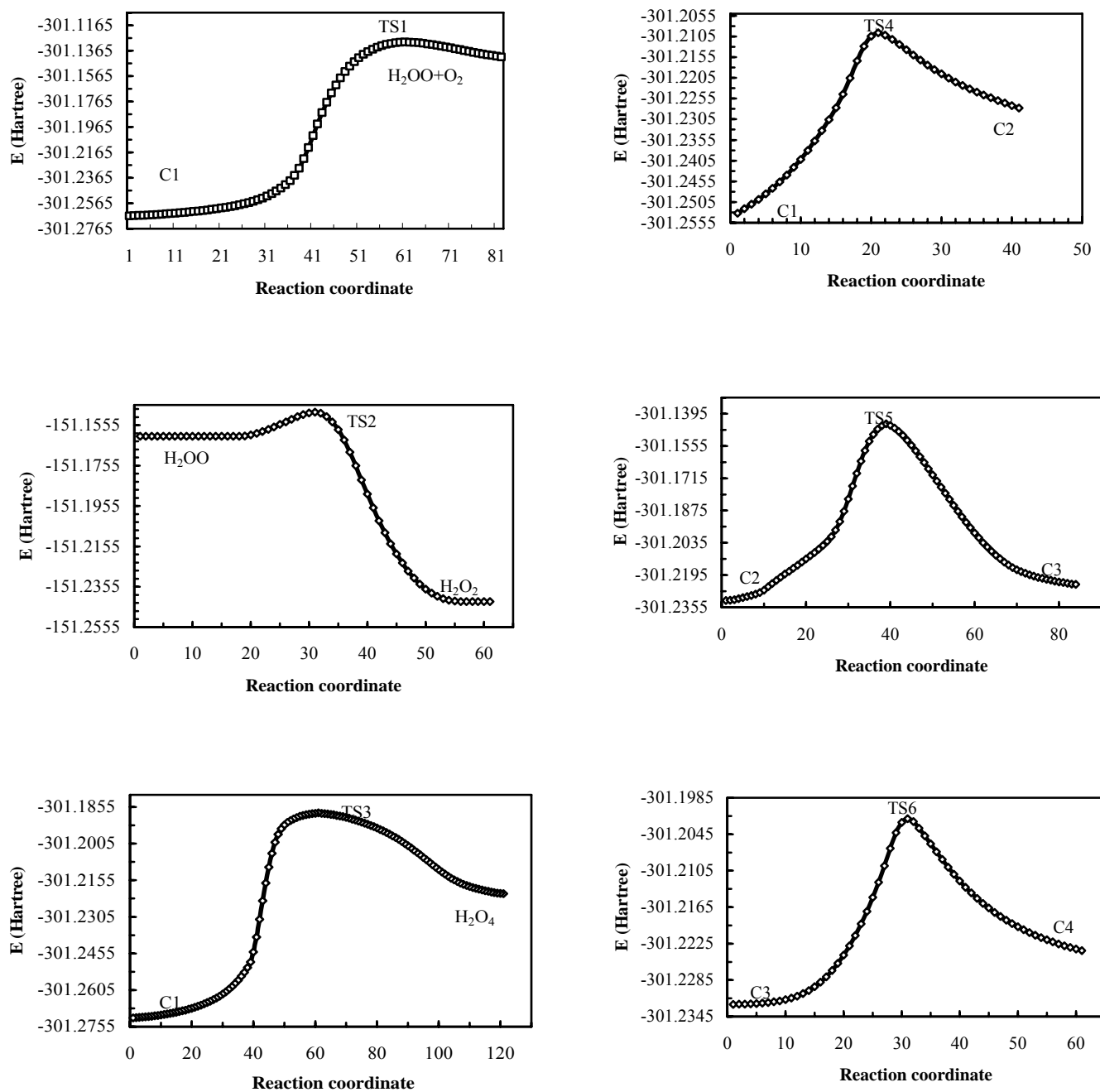


Fig. 4. The IRC curves for all the transition states that were calculated at the MP2/6-311++G(d,p).

IRC calculations for the formation of transition states from corresponding reactants are shown in Fig. 4 that confirms all reaction pathways.

For one O-abstraction and two H-abstraction reaction path taking place through TS1, TS3 and TS4, we have computed a barrier height of 354.972, 207.305 and 156.412 kJ mol⁻¹ relative to the separate reactants, respectively.

Thermochemistry

The change of thermodynamic properties for every reaction channel is different from the corresponding thermodynamic properties of products and reactants. Their value was corrected by ZPE for the H₂O + O₃ reaction. The calculated relative internal energies, enthalpies, Gibbs free energies and entropies of all steps of reactions in gas phase have been summarized in Table 4.

It can be seen from Table 4 that for channel (1), $\Delta E < 0$, $\Delta H < 0$, $\Delta G < 0$, at the MP2 method. These results show that

this channel spontaneously in the view of thermodynamic aspect. For channels 2 and 3, it can be seen from Table 4 that $\Delta E > 0$, $\Delta H > 0$ and $\Delta G > 0$. Thermodynamic parameters indicate that these channels are endothermic and non-spontaneous in gas phase. The changes of activation thermodynamic properties for various channels are the difference between the activation thermodynamic data of transition states and corresponding complexes, which are listed in Table 4 in italic form. The results indicate that the order of the relative enthalpy of activation for the three reaction channels is (1) > (2) > (3). All these data show that channel 3 has lower enthalpy of activation and free energy of activation.

CONCLUSIONS

The reaction of H₂O and O₃ was investigated at the Mp2/6-311++G(d,p) and CCSD/6-311++G(2df,2p)//MP2/6-311++

Table 4. Relative Energies ΔE , Enthalpies ΔH , Free Energies ΔG and Entropies $T\Delta S$, (kJmol⁻¹) for Reaction of Ozone and Water with ZPE Correction. The Activation Thermodynamics Data for Various Channels are Given in Italic

Channels	Reactions	ΔE	ΔH	ΔG	$T\Delta S$
R1	H ₂ O + O ₃ → C1	-7.284	-9.760	15.258	-25.019
	<i>C1 → TS1</i>	<i>362.524</i>	<i>362.524</i>	<i>370.0543</i>	<i>-7.530</i>
	TS1 → H ₂ OO + O ₂	-160.005	-157.529	-192.688	25.158
	<i>H₂OO + O₂ → TS2 + O₂</i>	<i>21.288</i>	<i>21.288</i>	<i>21.401</i>	<i>-0.112</i>
	TS2 + O ₂ → H ₂ O ₂ + O ₂	-236.040	-230.040	-235.138	60.223
	H ₂ O + O ₃ → H ₂ O ₂ + O ₂	-19.518	-19.518	-21.112	1.593
R2	<i>C1 → TS3</i>	<i>211.111</i>	<i>211.111</i>	<i>228.46</i>	<i>-17.349</i>
	TS3 → H ₂ O ₄ (HTO)	-84.468	-84.468	-84.864	0.397
	H ₂ O + O ₃ → H ₂ O ₄ (HTO)	<i>119.359</i>	<i>116.883</i>	<i>158.854</i>	<i>-41.970</i>
R3	<i>C1 → TS4</i>	<i>160.871</i>	<i>160.171</i>	<i>176.163</i>	<i>-15.290</i>
	TS4 → C2	-88.122	-88.122	-85.669	-2.455
	<i>C2 → TS5</i>	<i>248.898</i>	<i>248.898</i>	<i>243.734</i>	<i>5.166</i>
	TS5 → C3	-212.106	-212.106	-227.775	15.671
	<i>C3 → TS6</i>	<i>56.287</i>	<i>56.287</i>	<i>77.074</i>	<i>-20.789</i>
	TS6 → C4	-65.058	-65.058	-70.810	5.751
	C4 → 2HO ₂	116.744	119.220	73.365	45.856
	H ₂ O + O ₃ → 2HO ₂	210.230	210.230	201.338	8.891
	C2 → HO ₃ + OH	173.574	176.050	121.930	54.120
	H ₂ O + O ₃ → HO ₃ + OH	239.038	239.038	227.681	11.56

G(d,p) levels of theory. By dissociation of H₂O-O₃ complex, three product channels were found, one channel for O-abstraction from O₃ by H₂O and two channels for H-abstraction from H₂O by O₃ *via* corresponding transition states and complexes. AIM analyses were used to elucidate the reaction mechanism by comparing $\rho(r)$ of BCP in complexes and transition states. Furthermore, AIM indicates ring structure for some transition structures and complexes. Additionally, intrinsic reaction coordinate (IRC) calculation was performed to examine the correspondence of the calculated TS to the reactants and products. The thermodynamic results show that H₂O₂ + ³O₂ may be the main product of H₂O + O₃ reaction because of negative value of ΔG . As illustrated in PES (Fig. 3), H₂O₂ + ³O₂ as products are not produced from elementary reaction.

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