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Theoretical investigation study of Bromine radical reaction with ozone in stratospheric layer

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ABSTRACT

Theoretical study has been carried out to investigate the mechanism of reaction for bromine radical with ozone that's performed through PM3 of semi-empirical method. Geometry optimization and single point calculation through PM3-configuration interaction microstate have been done for all components of the suggested reaction and their transition states, in addition to vibrational analysis. The reaction of bromine radical with ozone is exothermic and spontaneously in the view of thermodynamic aspect. The energy barrier for this reaction $\Delta H^* < 0$, $\Delta G^* < 0$ and $\Delta S^* < 0$, that is indicated the proceeding of transition states are exothermic and spontaneous in gas phase at 298.15 K. The rate constant through TS1 equal to $k_{TS1} = 3.09 \times 10^9$ and $A_{TS1} = 1.413 \times 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at STP. While through TS4 equal to $k_{TS4} = 2.73 \times 10^{10}$ and $A_{TS4} = 1.209 \times 10^{13} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at STP.

Keywords: Bromine radical, ozone, potential energy surface, semi-empirical, and PM3.

INTRODUCTION

Ozone is the most important natural gas in the atmosphere and plays two critical roles -1. it removes most of the biologically harmful ultraviolet light before the light reaches the surface and 2. it plays an essential component in setting up the temperature structure, the heating/cooling balance in the atmosphere[1-5]. Bromine compounds from natural and anthropogenic sources play an important factor in the chemical processes of the atmosphere. Once these compounds are formed, photolysis and subsequent atmospheric oxidation processes release bromine radicals into the atmosphere [6]. The halo gases are depleting stratospheric ozone in catalytic cycles, which consists of two or more separate reactions. As a result, one bromine radical can destroy many thousands of ozone molecules before it reaches the stratosphere.

 $Br' + O_3 \rightarrow BrO + O_2$ (1)

Therefore, a little amount of reactive chlorine or bromine has a large impact on the ozone layer. This destruction occurs in the late winter/early spring season, where the large amount of most reactive gas is abundant. Chlorine monoxide or bromine oxide and chlorine or bromine radicals, leads to severe ozone

depletion. These gases participate in three principal reaction cycles that destroy ozone [7,8]. The importance of bromine and its chemistry in the atmosphere is receiving renewed interest based on the ability of bromine is almost 100 times more destructive to stratospheric ozone than chlorine atom [9,10].

The present study tend to investigate reasonable mechanism of Bromine radical reaction with ozone in stratospheric layer by using PM3 of semi-empirical calculation and to estimate the real transition state which is responsible for depleting reaction.

MATERIALS AND METHODS

Theoretical calculations were performed using computational implemented in the Hyperchem package 8.0.9 (2011) [11]. Optimized geometries of reactants, transition states and products with PM3-CI(4x4) [12,13]. Vibrational frequencies carried out through same methods to characterize the nature of stationary points with zero point energy [14]. Potential energy surface performed by mapping reactants into products to calculate the energy barrier [15].

RESULTS AND DISCUSSION

Table.1 shows the thermodynamic evaluation of reaction $Br^{\bullet}+O_3 \rightarrow BrO+O_2$. The results show that $\Delta E_r < 0$, $\Delta H_r < 0$, $\Delta G_r < 0$ and $\Delta S_r > 0$, therefore, this reaction is exothermic and spontaneous in the view of thermodynamic aspect [16]. From literature, it was found that the change in heat of formation for reaction $Br^{\bullet} + O_3 \rightarrow BrO + O_2$ equal to $\Delta H_r = -32.2 \text{ kCal mol}^{-1}$ at 298.15 K [17].

Table 1. Thermodynamic values change for the reaction $Br' + O_3 \rightarrow BrO + O_2$ calculated at PM3-CI (3×3) 298.15 K.

Thermodynamic change*	Br	O ₃	BrO	O_2	$\Delta_{ m reaction}$
Total energy $\times 10^3$	-8.1297	-20.1583	-14.8702	-13.4552	-37.4
Heat of formation	26.7	31.4	15.6	4.6	-36.9
Free energy	14.655	14.495	-0.083	-9.324	-38.557
Entropy	0.0404	0.0567	0.0526	0.0467	2.2×10^{-3}
Temp. x Entropy($T\Delta S$)	12.0453	16.905	15.683	13.924	

*measured in kCal/mol units

There are four suggested transition states for the reaction of bromine radical with ozone. Table .2 shows the comparative study in energetic properties of proposed transition states. The TS1 have higher zero point energy value (6.42 kCal mol⁻¹) than the other transition states, that means the TS1 has highest probability to transform into products $BrO+O_2$ with first negative imaginary frequency . In addition, the TS4 has 6.3 kCal mol⁻¹ of zero point energy with negative imaginary frequency but the energies of HOMO and LUMO deduced then, the TS1 has 122.2 kCal mol⁻¹ of energy gap whereas the TS4 has 132.63 kCal mol⁻¹. The TS1 needed lowest energy value of excitation than other transition states. The energy barrier value required for mapping reactants (Br + O₃) into TS1 is 3.9 kCal mol⁻¹, while 3.76 kCal mol⁻¹ for TS4.

Table 2. Energetic properties of proposed transition states of the Bromine and ozone reaction through first path way calculated at PM3-CI (3x3) method.

Type of Energetic	TS1	TS2	TS3	TS4
НОМО	-151.2	-150.05	-152.94	-155.93
LUMO	-29	-27.5	-23.6	-23.3
Eg	122.2	122.55	120.34	132.63
Dipole moment	1.401	2.259	3.251	2.77
Zero point energy	6.42	5.983	5.095	6.3
Imaginary frequency	-	+	+	+
Total energy $\times 10^3$	-28.3307	-28.3298	-28.3275	-28.3312
Total energy at S.T.P $\times 10^3$	-28.2732	-28.3098	-28.325453	-28.2738
Energy barrier(E _b)	3.9	-32.51	-47.97	3.76

*Energetic values in kCal/mol and Dipole moment in Debye (D) units. Geometry optimization of proposed structure transition states are shown in Figure.1



Figure 1: Geometry optimization of proposed structure transition states for bent ozone with bromine radical using PM3-CI(3x3) calculations.

The calculated enthalpies, free energies and entropies of all proposed transition states in gas phase have been summarized in Table 3. The results show that the TS1 has heat of formation equal to 13.06 kCal mol⁻¹ and TS4 has to be 13.63 kCal mol⁻¹. The free energy for all proposed transition states is G < 0 that can be referred to spontaneousness in the view of thermodynamic aspect in gas phase. The TS1 has higher free energy (G= -7.81 kCal mol⁻¹) at 298.15 K [18]. The changes in thermodynamic functions ($\Delta H^*, \Delta G^*$, and ΔS^*) for various transition states calculated by the difference between the thermodynamic data of transition states and reactants, which are listed in Table 3. The change of thermodynamic parameters ΔH^*

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< 0, $\Delta G^* < 0$ and $\Delta S^* < 0$ indicated that these transition states are exothermic and spontaneous in gas phase at 298.15 K [19]. The highest change in thermodynamic functions had been recorded with TS1 which indicate the TS1 and TS4 are most probable states to convert Br⁺+O₃ into BrO+O₂.

Table 3. Thermodynamics values for the	proposed transition states of the reaction $Br{+}O_3$ calculated
at PM3-CI(3×3) method at 298.15 K.	

Type of Energetic	TS1	TS2	TS3	TS4
Heat of formation(H)	13.06	14.235	17.94	13.63
Free energy(G)	-7.81	-7.143	-2.424	-5.45
Entropy(S)	0.07	0.0717	0.0683	0.065
Temp. x Entropy(TS)	20.87	21.38	20.364	19.38
Change of Enthalpy ΔH^*	-45.04	-43.865	-40.16	-44.47
Change of Free energy of ΔG^*	-36.96	-36.292	-31.574	-34.9
Change of Entropy ΔS^*	-0.0271	-0.0254	-0.0288	-0.0321
$T\Delta S^*$	-8.08	-7.573	-8.587	-9.57

*Energetic values in kCal/mol

The reaction $Br' + O_3 \rightarrow BrO+O_2$ is progresses, the non planar path way then follow planar path way. The bromine radical is attached to ozone molecule in non planar manner through TS1. As shown in Figure .3, TS1 has Br---O bond equal to 2.3 Å and the Br-O-O angle is 133.45° that indicate early transition state with high exothermicity equal to -45.04 kCal mol⁻¹at this step. The TS1 convert into TS2 to form bromine trioxide (BrOOO) with smallest angle equal to 104.7° than TS1and Br---O bond is contract from 2.3 to 1.8 Å which is more stable than TS1 and less energy than reactants . The TS2 is a planar intermediate and is less stable than products .That means the TS2 dissociated into products by cleavage of the central O–O bond. The TS4 have two nonplanar bonds interaction, first is 2.7 Å with 84.01° and second is 1.77 Å with 102.14°. The first Br---O bond directly convert into TS2 because it is the very early transition state with high exothermicity equal to -44.74 kCal mol⁻¹ at this step. That means the TS3 form behave as TS4. Finally, passage of TS1 or TS4 may be through TS2 to transit into products (BrO+O₂) as shown in the following equation -

$$BrO + O_3 \xrightarrow{TS1} TS2 \xrightarrow{TS2} BrO + O_2$$

Figure 2 shows the progress of reaction pass through the proposed transition states TS1 and TS4 which is used to calculate the rate constant.



Figure 2: The IRC curves for mapping reaction $Br' + O_3 \rightarrow BrO + O_2$ through proposed transition states calculated by PM3-CI(3x3).

Canonical Transition State Theory (CTST) that involves a semi-classical one-dimensional multiplicative tunneling correction factor [20]. The rate constants according to the CTST have the following expression:

$$k = \Gamma(T) \quad --- \quad --- \quad --- \quad --- \quad (2)$$

Where: $\Gamma(T)$ is the tunneling correction factor at temperature T. the Q_{TS}^* and Q_R are the total partition functions for the transition state and reactant per unit volume respectively. ΔE , k_B and h are the barrier height, Boltzmann's and Planck's constants respectively. The estimation of tunneling correction factor adopted the simple and computationally inexpensive Wigner's method using the following expression:

Where $v^{\#}$ is the imaginary frequency at the saddle point. The tunneling correction factor $\Gamma(T)$ is found to be almost unity. The partition functions for the transition state and reactant are obtained at 298.15 K from the harmonic vibrational frequencies [21,22]. The rate constant curve of reaction $Br^{\bullet} + O_3 \rightarrow BrO + O_2$ through proposed TS1 and TS4 are given in figure 3. The calculated Arrhenius constant (A_{TS1}) from figure-3A of reaction $Br + O_3 \rightarrow TS1$ equal to $A_{TS1}=1.413 \times 10^{12} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ and rate constant is $k_{TS1}=$ $3.09 \times 10^9 \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ at STP with activation energy equal to 3.9 kCal/mol. While the calculated rate constant from figure- 3B of reaction $Br + O_3 \rightarrow TS4$ equal to $k_{TS4}=2.73 \times 10^{10} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ and Arrhenius constant is $A_{TS4}=1.209 \times 10^{13} \text{ mol}^{-1} \text{dm}^3 \text{s}^{-1}$ at STP with 3.76 kCal/mol of energy barrier. Rate constant for proposed forward reaction through first path way calculated by PM3-CI (3x3) is shown in figure 3



Figure 3: Rate constant for proposed forward reaction through first path way calculated by PM3-CI (3x3) between 200 and 1000K. A - Br' + O₃ \rightarrow TS1 B - Br' + O₃ \rightarrow TS4

APPLICATIONS

Theoretical study is useful to investigate the mechanism of reaction for bromine radical with ozone that is performed through PM3 of semi-empirical method. The reaction of bromine radical with ozone is exothermic and spontaneous in the view of thermodynamic aspect. The proceeding of transition states are exothermic and spontaneous in gas phase at 298.15 K.

CONCLUSIONS

The reaction of Bromine radical with ozone in stratospheric layer is exothermic and spontaneous in the view of thermodynamic aspect. The energy barrier for this reaction is 3.9 kCal mol⁻¹ through TS1, while 3.76 kCal mol⁻¹ through TS4. The thermodynamic of activation $\Delta H^* < 0$, $\Delta G^* < 0$ and $\Delta S^* < 0$ indicated that these transition states are exothermic and spontaneous in gas phase at 298.15 K. The rate constant through TS1 is k_{TS1} = 3.09×10⁹ and A_{TS1} =1.413×10¹² mol⁻¹dm³s⁻¹ at STP . While through TS4 equal to k_{TS4} = 2.73×10¹⁰ and A_{TS4} = 1.209×10¹³ mol⁻¹dm³s⁻¹ at STP.

REFERENCES

- [1] World Meteorological Organization (WMO), Scientific assessment of ozone depletion: **1991**, WMO Global Ozone Res. and Monit. Proj. Rep. 25, **1992**.
- [2] D. J. Chartrand, J. de Grandpré, J. C. McConnell, *Atmosphere-Ocean*, **1999**, 37(4), 309–367.
- [3] A. C. Voukides, K. M. Konrad, R. P. Johnson, J. Org. Chem., 2009, 74(5), 2108-2113.
- [4] M. A. Mendes, L. A. B. Moraes, R. Sparrapan, M. N. Eberlin, R. Kostiainen, T. Kotiaho, J. Am. Chem. Soc., 1998, 120(31), 7869-7874.
- [5] S. Pekárek, Eur. Phys. J. D, 2010, 56, 91–98.
- [6] J. C. Hansen, Y. Li, and J. S. Francisco, Z. Li, J. Phys. Chem. A, 1999, 103(42), 8543-8546.
- [7] A. J. G. Baumgaertner, P. Jöckel, H. Riede, G. Stiller, B. Funke, *Atmos. Chem. Phys.*, **2010**,10, 7285–7302.
- [8] C. H. Jackman, R. D. McPeter, *Geophys. Mon.*, 2004, 141, 305–31.

- [9] W. S. McGivern, O. Sorkhabi, A. G. Suits, A. Derecskei-Kovacs , S.W. North, *J. Phys. Chem. A*, **2004**, 104, 45.
- [10] V. L. Orkin, F. Louis, R. E. Huie, M. J. Kurylo, J. Phys. Chem. A, 2002, 106, 43.
- [11] HyperChemTM 8.0.9. for windows molecular modeling system, Hypercupe, Inc., **2011**.
- [12] I. Sheikhshoaie, S. Saeednia, *The Arabian Journal for Science and Engineering*, **2010**, 35 (1A), 53-60.
- [13] D. Margeti, R. N. Warrener, Croat. Chem. Acta, 2003, 76 (4), 357–363.
- [14] F.H.Hussen, M.H.Obes, A. A. Drea, *Int. J. Chem. Sci.*, **2010**, 8(4), 2763-2774.
- [15] M.H.Obes, A. A. Drea and F.H.Hussen, Int. J. Chem. Sci., 2012, 10(1), 63-79,.
- [16] P.W. Atkins, and J. de Paula, "*Physical Chemistry for the Life Sciences*", *New York*, W. H. Freeman and Company, 2006.
- [17] Z. Li, J. Phys. Chem. A, **1999**, 103(9), 1206-1213.
- [18] M. Tozihia, M. Vahedpoura, F. Nazarib, J. Iran. Chem. Soc., 2010, 7(3), 585-596.
- [19] D. Y. Hwang, A. M. Mebel, J. Chem. Phys., 1998, 109(24),10847-10851.
- [20] À. González-Lafont, J. M. Lluch, A. Varela-Álvarez, J. A. Sordo, J. Phys. Chem. B, 2008, 112(2), 328–335.
- [21] D. C. Young, "Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems", New York, John Wiley & Sons, Inc, **2001**.
- [22] C. J. Cramer, "Essentials of Computational Chemistry: Theories and Models", 2nd Ed., John Wiley & Sons Ltd, **2004**.