Computational study on the potential energy surface for the reaction HO₂ + NO

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Abstract: The reaction between two radicals HO₂ and NO plays a key role in both atmospheric and combustion chemistry [1, 2], relevant to several environmental concerns. In this work, the gas-phase chemical reaction HO₂ + NO has been investigated by state-of-the-art ab initio calculations. The rigorous singlet potential energy surface (PES) was constructed at accurate composite CBS-QB3 level of theory, which reveals the three possible pathways for the formation of HO + NO₂ from HO₂ + NO: (i) the direct oxygen abstraction reaction which is the novel pathway, or (ii) the direct O-O dissociation of the peroxynitrous acid, HOONO intermediate, or (iii) the O-N bond breaking reaction after the isomerization of HOONO to nitric acid (HO-NO₂). Multiple pathways was explored to occur via isomerization and decomposition reactions of HOONO intermediate leading to a variety of intermediates and products, HNO + O₂, HON + O₂, and HONO + O. Our result indicates that nitric acid HO-NO₂ is thermodynamically the most stable species followed by the peroxynitrous acid HOONO. The calculated bond lengths, harmonic vibrational frequencies, and the bond dissociation energy for cis,cis-HOONO are in good agreement with available theoretical and experiment data. Our predicted data are valuable information for further investigation on a detailed kinetic analysis of this system.

Keywords: Combustion and Atmospheric Chemistry, Potential Energy Surface, HO₂, NO, Radicals, CBS-QB3

Introduction:
Two radicals HO₂ and NO are crucial chemical molecules in the field of atmospheric and combustion chemistry [1, 2].

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{HOONO} \quad (1) \\
\text{HOONO} & \rightarrow \text{OH} + \text{NO}_2 \quad (2) \\
\text{HOONO} & \rightarrow \text{HNO}_3 \quad (3)
\end{align*}
\]

Not only involving in ozone and other air pollutants (NOₓ gasses) cycles but the reaction HO₂ + NO also contributes to an increase in nitric acid (HNO₃) deposition. Due to their direct relationship to vital environmental issues like global warming, the formation of atmospheric acid, particularly HNO₃, and ozone production and depletion, kinetics of the reaction between these two radicals has attracted numerous experimental and theoretical groups of investigators [3-25]. Theoretically, Sumathi and Peyerrimhoff studied this reaction at the B3LYP/6-311++G(d,p) level of theory with some species reported at the MP2/6-311++G(d,p) and identified different possible product channels, HO + NO₂, HO-NO₂, HNO + O₂, and NOH + O₂. Later, Lin and co-workers [12, 14] carried out theoretical studies of this system in more detail by both the forward and the reverse processes using the highest scheme of G2M method and concluded HO + NO₂ is dominant product occurred via two pathways. The direct fragmentation of HOONO intermediate to HO + NO₂ is more favorable than its isomerization to nitric acid HO-NO₂. Recently, the full-dimensional PES for this system was also studied by Chen et al. using quasiclassical trajectory calculations [20, 22]. Additionally, Butkovskaya and co-workers [15, 17] focused on the study HNO₃ forming channel from HO₂+NO reaction both experimentally and theoretically. They indicated that both cis,cis-HOONO and the more stable product HO-NO₂ were detected in the experiment. To the best of our knowledge, only a few theoretical studies investigated on the full potential energy surface (PES) for the title reaction and its PES has not yet been presented thoroughly. To better control the effects of this reaction on atmosphere and combustion, we perform an exhaustive study of this system based on all data available in the literature.

The present study aims at characterizing an accurate and complete singlet PES of the gas-phase reaction of HO₂ radical with NO using high-level composite method CBS-QB3. Then, geometrical parameters including bond lengths, harmonic vibrational frequencies, and bond dissociation energy will be compared with previous theoretical data and existing experimental values. Besides, all pathways will be depicted to elucidate the whole mechanism for the reaction of HO₂ + NO.

Computational Methods:
All calculations were carried out with the Gaussian-09 program package [26, 27]. For the sake of high accuracy and efficient computational time, the composite CBS-QB3 method by George Petersson and co-workers [28] was utilized since its accuracy is...
within ~ 1 kcal/mol of the experimental value. The geometries and frequencies of reactants, products, intermediates and transition states of the title reaction were fully optimized by using the hybrid density functional B3LYP method (Becke’s three parameters nonlocal exchange functional with the correlation function of Lee, Yang, and Parr) with the split-valence polarized basis set 6-311++G(2d,p). Afterward, the single point energies were refined by extrapolating to the infinite basis set limit after performing several levels of theory consisting of CCSD(T)/6-31+G(d,p) and MP4SDQ/CBSB4. All presented data for ground state molecules and transition states (first-order saddle points on the PES) were selected for the lowest-energy conformer of a given species. Vibrational frequencies were analyzed to characterize stationary points. Only one imaginary frequency in the vibration modes analysis was identified for the transition state geometries whereas no imaginary frequency was found for reactants, products, and intermediates. Intrinsic reaction coordinate (IRC) calculations were also employed to confirm the connection of each transition state with designated intermediates via minimum energy path (MEP) [29].

In this study, some low-frequency vibrational modes, which are better treated as internal rotations around single bonds, were explicitly evaluated the hindered internal rotations (HIR) in the most accurate manner as described below. The 1-D Schrödinger equation for a hindered internal rotor (HIR) is given as

$$\frac{-1}{2l_{\text{red}}} \frac{d^2 \Psi_{\text{hir}}}{dx^2} + V(\theta)\Psi_{\text{hir}} = E\Psi_{\text{hir}}$$

where E is the energy and l_{\text{red}} is the reduced moment of inertia for the considered rotation and is calculated as I according to East and Radom [30] on the basis of the original work by Kilpatrick and Pitzer [31]. The hindrance potential, V(\theta), is directly computed as a function of torsional angle, \theta, with a step of 10°. Specifically for this system, it was obtained at the B3LYP/CBSB7 level via relaxed surface scans with the step size of 10 degrees for dihedral angles that correspond to the rotations. To solve the HIR equation, we cast it into a Mathieu-type equation by representing the hindrance function as a Fourier series, \[ V(\theta) = \sum_{i=-L}^{L} C_i e^{i\theta} \], in which L is some cut-off number depending on the nature of the potential. The wave function was expanded as a harmonic series, \[ |m\rangle = \frac{1}{\sqrt{2\pi}} e^{i m\theta} \], and plugged into HIR equation. The matrix elements of the Hamiltonian are then given by

$$H_{mm} \equiv \langle m|H|n \rangle = \frac{1}{2\pi} \int_{0}^{2\pi} e^{-im\theta}$$

$$\times \left[ \frac{1}{2l_{\text{red}}} \frac{\theta^2}{d\theta^2} + \sum_{i=-L}^{L} C_i e^{i\theta} \right] e^{in\theta} d\theta$$

The matrix can be diagonalized to obtain its eigenvalue spectra which are the energy levels of the considered rotor. Further details of our method of research can be found in the previous paper by Mai et al. [32].

**Results and Discussion:**

The potential energy diagram for the reaction between HO₂ radical and NO radical was extensively explored obtained at 0 K using CBS-QB3 level of theory, presented in Figure 1. Geometries of all species with important geometrical parameters were optimized at the CBS-QB3 level of theory. To facilitate the discussion, the CBS-QB3 values are used universally and the energies are cited relative to that of the reactants; otherwise, it will be explicitly stated.

**Figure 1** presents the singlet potential energy surface of the HO₂ and NO reaction forming an internally-energized adduct cis,cis peroxynitrous acid: HOONO (I₁) by the O-N bond formation between HO₂ and NO radicals. This process occurs barrierlessly with high exothermicity (ΔH = -26.5 kcal/mol). Three stable peroxynitrous acid HOONO isomers, namely cis,cis-HOONO (I₁), trans,perp-HOONO (I₂), cis,perp-HOONO (I₃), exist as the same prediction of several previous research groups [11, 14, 33-36]. In addition, cis,cis-HOONO (I₁) is the most stable species among them, which was also predicted by all the authors [12, 14-17, 20, 21]. The relative energies of the three isomers I₁, I₂, and I₃ are 0.0, 2.9, and 0.9 kcal/mol at CBS-QB3 level, which is close to the corresponding values of 0.0, 2.5 and 0.6 kcal/mol obtained at the G2M (CC1) level [14].

Like all other research groups, our study indicates that cis,cis-HOONO conformer is the lowest energy structure among all peroxynitrous acid conformers. The geometry of optimized cis,cis-HOONO including calculated bond lengths and bond angles is presented in Figure 2. By comparison to the QCISD and G2M results [14, 24], which are also showed in Figure 2, our structure demonstrates the similar geometry of the most stable peroxynitrous acid cis,cis-HOONO. Both bond lengths and bond angles at three levels are almost identical. Moreover, CBS-QB3 harmonic vibrational frequencies have been summarized in Table I. It can be seen that our predicted CBS-QB3 frequencies are close to those from other theoretical and experimental data. For the bond dissociation energies (BDEs), D₀ (HO-NOO) for the cis,cis-HOONO (I₁) predicted at 0 K is 18.7 kcal/mol at CBS-QB3 level. This is close to the experimental value, D₀ (HO-NOO) = 19.8 ± 0.23 kcal/mol [23] and 20.5 kcal/mol predicted at G2M level [14]. Meanwhile, the calculated bond energy D₀ (HOO-NO) is 26.3 kcal/mol for I₁, which is close to 28.7 kcal/mol obtained at G2M level [14].
Three stable peroxynitrous acid HOONO isomers $\mathbf{I_1}$, $\mathbf{I_2}$, and $\mathbf{I_3}$ can isomerize each other. At the CBS-QB3 level, the isomerization barrier height from $\mathbf{I_1}$ to $\mathbf{I_3}$ via TS1_3 is only 0.4 kcal/mol undergoing the hinder internal rotation around the O-O bond. Because of its small barrier, $\mathbf{I_3}$ is not showed in Figure 1 for simplification and is included as internal rotation. However, from $\mathbf{I_1}$ to $\mathbf{I_2}$, it has to overcome 12.9 kcal/mol barrier via TS1_2 by rotating around O-N bond. These barrier energies (0.4 and 12.9 kcal/mol) agree well with the values 0.6 and 12.6 kcal/mol [14] obtained at the G2M level respectively. Additionally, the optical isomers $\mathbf{I_2}$ and $\mathbf{I_2'}$, and $\mathbf{I_3}$ and $\mathbf{I_3'}$ have exactly the same energies in this study, which is consistent with Zhu and Lin study at G2M level [14].

**Figure 1.** The schematic diagram of the potential energy surface for the HO$_2$ + NO system computed at 0 K using CBS-QB3 level of theory. Numbers are in kcal/mol.

**Figure 2.** Optimized geometry (bond distances in Å and angles in degrees) of cis,cis-HOONO at CBS-QB3 level of theory. The numbers in the parentheses are calculated values at QCISD/cc-pVDZ level from the work of Francisco et al. [24] and numbers in the square brackets are G2M values from the work of Lin et al. [14].

**Table 1.** Harmonic vibrational frequencies (in cm$^{-1}$) for cis,cis-HOONO.

<table>
<thead>
<tr>
<th></th>
<th>CBS-QB3$^a$</th>
<th>QCISD/cc-pVDZ$^b$</th>
<th>G2M$^c$</th>
<th>Exptl$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathbf{I_1}$</td>
<td>333.2</td>
<td>335</td>
<td>355.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>374.6</td>
<td>411</td>
<td>373.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>507.2</td>
<td>506</td>
<td>512.5</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>646.0</td>
<td>671</td>
<td>664.6</td>
<td>629.1</td>
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<tr>
<td></td>
<td>840.4</td>
<td>839</td>
<td>845.5</td>
<td>794.3</td>
</tr>
<tr>
<td></td>
<td>963.6</td>
<td>974</td>
<td>966.8</td>
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</tr>
<tr>
<td></td>
<td>1454.8</td>
<td>1484</td>
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<tr>
<td></td>
<td>1675.8</td>
<td>1706</td>
<td>1667.0</td>
<td>1600.3</td>
</tr>
<tr>
<td></td>
<td>3519.5</td>
<td>3563</td>
<td>3532.4</td>
<td>3285.4</td>
</tr>
</tbody>
</table>

$^a$ This work
$^b$ QCISD/cc-pVDZ values from the work of Francisco et al. [24]
$^c$ G2M values from the work of Lin et al. [14]
$^d$ From the experimental work of Lo and Lee. [25]
From the most stable adduct 11, many possible channels such as isomerization and dissociation reactions can undergo to form HO + NO2 (P1), HNO + O2 (P2), HON + O2 (P3), HOHO + O (P4). All channels are depicted as followings:

(1) \( \text{HO} + \text{NO}_2 \) (P1) formation

The direct dissociation of \( \text{cis,cis-HOONO} \) (11) results in \( \text{HO} + \text{NO}_2 \) (P1) formation lying at -8.0 kcal/mol by breaking of the O-O bond in hydroperoxyl group of 11 with a barrier of 18.7 kcal/mol. Besides, 11 can isomerize to give nitric acid HO-NO2 (18) which is the most stable intermediate in this system via TS1_8 lying 23.6 kcal/mol above HOONO, or 4.9 kcal/mol higher than the energy of the dissociation product, HO + NO2.

(2) \( \text{HNO} + \text{O}_2 \) (P2*) formation

As seen from Figure 1, the breaking of the O-N bond from two possible pathways to form \( \text{HNO} + \text{O}_2 \) by direct decomposition of intermediate either 111 or \( \text{I12} \) with barrier energies of 16.6 and 16.8 kcal/mol, respectively. \( \text{I12} \) can be formed through H migration from I2 to the N atom of the nitric oxide with 46.5 kcal/mol barrier. \( \text{I11} \) and \( \text{I12} \) are connected by TS11_12 lying 12.9 kcal/mol above \( \text{I12} \), which corresponds to the rotation of the O-O group around the N-O bond. From \( \text{I11} \), isomer \( \text{I10} \) is produced with through H migration from O atom to another O atom of hydroperoxyl group with a barrier height of 53.3 kcal/mol; this \( \text{I10} \) can further connect to \( \text{I11} \) via TS10_11 with 38.7 kcal/mol barrier.

(3) \( \text{HON} + \text{O}_2 \) (P3) formation

Similarly, \( \text{HON} + \text{O}_2 \) formation occurs in two channels from intermediate either 14 or 15 by breaking O-N bond with barrier energies of 30.7 and 27.3 kcal/mol, respectively. 11 and 14 are connected by TS1_4 through H migration from I11 to N atom of nitric oxide with 41.9 kcal/mol above I11.

(4) \( \text{HOONO} + \text{O} \) (P4) formation

From Figure 1, HO-NO2 (I18) can isomerize to intermediate I17 via TS7_8 lying 96.2 kcal/mol. Then, I17 can directly dissociate to \( \text{HONO} + \text{O} \) by overcoming 9.6 kcal/mol via a triplet transition state or isomerize to 14 or 15 with a much higher barrier (31.5 and 19.3 kcal/mol above I17, respectively).

Figure 1 also shows that there are two possible direct abstraction channels, \( \text{HO}_2 + \text{NO}_2 \rightarrow \text{HO} + \text{NO}_2 \) (P1) and \( \text{HO} + \text{NO}_2 \rightarrow \text{HONO} + \text{O}_2 \) (P2), via two triplet transition states with barrier heights of 16.3 and 29.1 kcal/mol respectively. In spite of the high barrier (29.1 kcal/mol) of the novel triplet transition state for the direct oxygen abstraction, it needs further study on its effect on the kinetic of this system.

Due to the requirement of high isomerization barriers, \( \text{P2, P2*, P3, and P4} \) formation are kinetically expected to play less important role comparing to the low-energy lying channel HO + NO2 (P1) formation which is -8.0 kcal/mol lower in energy than the reactant radicals. Hence, P1 is considered as a thermodynamically favorable product.

Conclusion:

The detailed reaction mechanism for HO2 + NO system has been extensively constructed using a highly accurate method CBS-QB3. From our results, we draw following conclusions:

(1) Our optimized structure of \( \text{cis,cis-HOONO} \) is predicted similar to the previous studies in terms of bond lengths, bond angles, bond dissociation energies, and vibrational frequencies.

(2) Three possible pathways can lead to HO + NO2 product (P1) from HO2 + NO. The direct oxygen abstraction is the new pathway in this study compare to the previous studies. P1 can also be produced by either two-step via the direct O-O dissociation of the peroxyxynitrous acid, cis,cis-HOONO I11 or three-step mechanism that I1 isomerizes to nitric acid I18 then dissociates to form P1.

(3) Among several possible product channels, the formation OH + NO2 product (P1) is dominant due to its low energy 8 kcal/mol less than the energy of reactants.

A good agreement between our data and other theoretical values and experiment data makes us more confident on our results which are valuable and important to further study on detailed kinetics for this system.

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References:


