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Allowed energetic pathways for the three-body recombination reaction of nitrogen monoxide with the hydroxyl radical and their potential atmospheric implications

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ABSTRACT: The OH initiated oxidation of nitric oxide (NO) is an important atmospheric reaction being, during the day time, the main channel that leads to the formation of HONO a reservoir species for both OH and odd nitrogen. This work reports ab initio study of the Potential Energy Surface (PES) of NO + OH using density functional theory calculations conducted at the B3LYP level of theory with a 6-311g (d,p) basis set. We confirmed experimental observations pointing out that the main channel for this reaction is the formation the HONO. From the addition of OH to NO both cis and trans isomers of HONO were found to be the formed as stable intermediate, both having a negative enthalpy of formation relative to the reactants, the cis isomer being more stable than the trans one. The ab initio calculations were extended to include the hydrogen extraction mechanism with its respective transition state to investigate the potential existence of a reaction channel leading to the formation of $NO_2 + H$, that was found not to be of significant interest.

Keywords: ab initio calculations; HONO; nitric oxide; hydroxyl radical

Introduction

Nitrous Acid HONO is an atmospheric constituent important in urban contexts being a reservoir species both for OH and odd nitrogen [1-5]. During the day HONO is formed in the OH initiated oxidation of Nitrogen Monoxide, but it quickly decomposes back into reactants via a photolytic process. At nighttime, in absence of a light source, HONO is produced via different dark reactions and accumulates both in gaseous and liquid phases effectively creating a reservoir for both OH and NO. In the early morning

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hours the sun comes up again over the horizon photolyzing progressively, as it rises toward the zenith, HONO. It has been estimated that OH early morning production due to HONO photolysis may account to up to 60% of the overall tropospheric OH budget kickstarting in turn the tropospheric chemistry of the daytime [6-8]. Another reason to look into the allowed pathways for the title reaction is HONO has been used as precursor for the hydroxyl radical in laboratory studies [9-11].

One of the main accepted mechanisms for the formation of HONO is the three body recombination reaction of the hydroxyl radical with nitric oxide [12]:

$$OH+ NO+ (M) \rightarrow HONO + (M^*)$$
(1)

Reaction (1) it is not a simple mechanism but occurs via a three steps process that can be broken down as:

$OH + NO \rightarrow HONO^*$	(2a)
	· · ·

$$HONO^* \rightarrow OH + NO$$
 (2b)

$$HONO^* + (M) \rightarrow HONO + (M^*)$$
(3)

Reaction (2a) is the reversible addition of OH to the NO radical with the formation of an energized adduct indicated as HONO*. The adduct so formed can either redecompose back into the reactants (2b) due to its lack of ability to store the excess energy or can be stabilized by the transfer of said excess energy to a third body M, dissipating in this way at least part of the energized adduct.

Recent field studies [6-8] have focused their attention on evaluating the impact of nitrous acid (HNO_2 or HONO) photolysis on the overall OH tropospheric budget. The interpretation of the field measurements seems to point out that under certain conditions mainly related to the polluted and urban environment the relative importance of nitrous acid as precursor of the hydroxyl radical are much larger as a percentage than what previously estimated [13-14].

The kinetic community has shown significant interest in reaction (1) [14-29]. As shown in Fig. 1 an accurate determination for the rate of recombination for the OH initiated oxidation of nitrogen monoxide has been recently determined by Pulsed Laser Photofragmentation-Laser Induced Fluorescence (PLP-LIF) [12] in the range of pressure and temperature characteristic of the troposphere, notwithstanding a lack of information on the geometry and the structure of the reaction product. It has been hypothesized that the yield in HONO for the title reaction is 0.8 [25], but little work has been done in investigating the potential reaction pathways allowed for this reaction. These observations have renewed our interest for the title reaction. Our main goal in this study was to check for possible allowed reaction pathways for the recombination of OH with NO

and clarify the structure of what was thought to be the main product: HONO.

Material and Methods

The present study reports ab initio calculation on the formation of HONO from gas phase reaction between the hydroxyl radical and nitric oxide. The goal of this study is to clarify the nature of the products for the title reaction and predict verifiable vibrational frequencies that can be scrubbed against literature data or in separate laboratory work to validate our conclusions. The Density Functional Theory employed in this study is at the B3LYP level of theory with a 6-311g (d,p) basis set. Density Functional Theory is a computational method that solves the electronic (time-independent) Schrödinger equation, with atomic structure (internal coordinates) as variables. In this method, molecular geometry is proportional to Energy, with varying functions of bond distance, bond angles, and dihedral angles, resulting in a gradient of Energy with specific coordinates. That Energy is minimized, resulting in an equilibrium situation reflecting optimized coordinates. A consequence of this equilibrium coordinate calculation is the determination of vibrational frequencies, which is also reported in this study and can be measured experimentally. B3LYP is a type of Density Functional Theory, which accounts for relativistic effects from other electrons in sub shells. B3LYP is widely accepted in the theoretical chemistry community as an accurate (within 1-2 kcal/mol) ab initio PES method. 6-311g (d,p) is a basis set to the functional employed in Density Functional Theory [30-32].

All optimized cartesian geometries, relative energies, zero-point energy, rotational constants, moments of inertia, and harmonic frequencies were performed at the B3LYP/6-311G(d,p) level of theory using Gaussian 98 *ab initio* software [33]. In order to perform a constrained optimization of the PES for the present reaction path forming algorithm the energy is expressed as the Taylor expansion:

$$E=E'+gT * \Delta x + 0.5 \Delta x * H * \Delta x + ...$$
(4)

Where E' is the energy at a point x' on a sphere of radius 0.5 s centered at x, g is the gradient and H is the Hessian operator. Gaussian algorithm provides for self consistent field values for the Energy values including the TS energy by starting with the analytical Hessian equation for the transition state:

$$H'=H''+(\Delta g' * \Delta g'')/(\Delta g' * \Delta x') - (H'' * \Delta x') * (\Delta x'^{T} * H'')/(\Delta x'^{T} * H * \Delta x')$$
(5)

where $\Delta g'=g'-g''$, $\Delta x'=x'-x''$ and the superscripts ' and " refer respectively to the current and previous points. The algorithms provided are iterated over and over according to the self consistent field theory to minimize the differences between the valued for the energies at the current and previous point *via* an iterative process. Detailed explanation of the Gaussian 98 algorithm is found in Gonzalez and Schlegel [36-37].



Figure 1. Absolute rate coefficient for the gas phase recombination of OH with NO in Nitrogen, (\bullet) [12]; (\Box) [29]; (\circ) [24]; (\Box) [38] (Δ) [18].; The solid line represents the curve produced using the NASA-JPL, 2003 parametrization; the dashed line is the IUPAC, 1997; and the dotted line is the IUPAC 2003.

At the B3LYP/6-311g(d,p) level, TS HONO has only one imaginary vibrational frequency, whose vibrational vector corresponds to the H translational motion leading to *cis*-HONO and *trans*-HONO. IRC calculations at this level of theory were carried out on TS HONO, confirming that this transition state is the saddle point that connects to *cis*-HONO to *trans*-HONO on its surface [34-35].

Results and Discussion

In this study, the Energies of NO and OH, both radical species with an unpaired electron, were determined. The combined Energy of NO and OH were set to zero, to create an arbitrary scale for the PES. All intermediates, transition states, and products Energy's was mapped relative (Erel) to this zero energy of the reactants. Table 1 shows the Erel of all species studied. The intermediates examined are NOOH, *cis*-HONO, *trans*-HONO, and HNOO. The only thermodynamically favorable intermediate that resulted were *cis*-HONO (-46.2 kcal/mol) and *trans*-HONO (-45.9 kcal/mol). These results are generally in agreement with previous literature data [38,39] but place in evidence that the role of the *cis* isomer may be more important than what previously assumed. Intuitively one would expect the *trans* isomer to be more stable because of sterical reason, but according to our calculation for this particular molecule the *cis* isomer seems to have a slightly deeper (Δ E approx. -0.3 kcal/mol) well. Either way such small difference only points out that the main product for the title reaction is in fact a mix of *cis*

and *trans* HONO rapidly interconverting one into each other with a slight prevalence of the *cis* one.

The stability of these two intermediates is based on the fact that both of them are stable species with no unpaired electrons. All of the other intermediates are radicals, and as such, a higher energy would be expected. Hence according to our *ab initio* study the net equation then is:

$$NO + OH \rightarrow HONO$$
 (1)

A transition state between *cis*-HONO and trans-HONO was located (labeled as TS HONO). The geometry of its terminal H lies in the plane of O-N on the HONO surface, serving as a "half-way point" between the *cis*-HONO and *trans*-HONO isomers. The Erel of TS HONO is at -34.3 kcal/mol, suggesting the *cis*-HONO and *trans*-HONO readily go isomerization to one another, relative to the reactants thermodynamic conditions. No other transition states were located since all intermediates. Also, this and all transition states contain an imaginary frequency. Intrinsic Reaction Coordinates (IRC) were not performed since the TS involved are H shifts. For the purpose of this study it was sufficient to find the TS as a half-way point in terms of geometry between two intermediates. It is understood that the H geometry of the TS followed geometrically to those intermediates, and serves as barriers.

				== 3(*/*/		
	NO	ОН	NO+OH	NOOH	ΗΟΝΟ	HNOO
E*	-129.92217	-75.74609	-205.66826	-205.66522	-205.74190	-205.62061
ΔE			0.00000	0.00304	-0.07364	0.04765
E			0.00000	1.90512	-46.20792	29.90209
[cal/mol]						
E*	HNOO	HONO	ONO	н	ts	HNO
	(linear)	(t)				
ΔE	-205.406946	-	-205.626059	-0.502156	-205.697004	-130.38739
		205.741469				
E	0.26131	-0.07321	0.04220	205.16610	-0.02874	75.28087
[cal/mol]						
E* _	163.97641	-45.93998	26.48090	128743.69718	-18.03776	47239.46599

Table 1. Energy and Erel of all species considered in the *ab initio* calculations reported in the present paper. (*)calculated using b3lyp/6-311g(d,p)

A possible product that can develop from the NO + OH reaction is the ONO species, this channel may be relevant and it has been included in our calculations due the high energetic stability of the NO_2 molecule. H + ONO is the result after a proton extraction of HONO. If the channel leading to the formation of hydrogen atom and nitrogen dioxide would be energetically allowed then on of the possible reaction's channel would be the following:

$$NO + OH \rightarrow H + ONO$$
(3)

The pathway to ONO would be from the HONO route, so the overall reaction

scheme is:

$$NO + OH \leftrightarrow HONO \rightarrow H + ONO$$
 (6)

This route is examined to verify whether HONO is the prevailing product or if the channel leading to the dissociation of the product into H + ONO is rather an energetically comparable alternative. The proton extraction that leads to ONO formation comes from a H-ONO transition state (labeled TS ONO). According to the results of our calculations as reported in Table 2 together with the molecular geometries, reaction coordinates, and vibrational , the NO₂ formation is an energetically prohibited channel for this reaction. The H-ONO transition can form from either *cis*-HONO or *trans*-HONO, at -18.0 kcal/mol but the proton extraction proceeds the H-ONO transition formation, resulting in ONO as a product (at 26.5 kcal/mol). Having a H + ONO product with an energy barrier relative to the reactants suggests that H + ONO does not develop, and indeed the net general reaction scheme remain:

$$NO + OH \rightarrow HONO \tag{1}$$

The decomposition of the *trans* isomer back into the reactants has also been object of a recent theoretical study by Bauerfeldt and its group [40]. Despite considering only the decomposition of the *trans* isomer in the $(X^{1}A')$ state into the reagents for reaction (1) at a higher level of theory, their conclusions seems to be in general agreement with the calculations reported in the present paper confirming the general validity of our conclusion.

A careful comparison between this work and other *ab initio* studies including ref. [35] can be made by looking at the vibrational frequencies predicted by the different sets of calculations for the *trans*-HONO and the experimental values currently accepted in the literature [38-40]. Said comparison is shown in Table 3 and serves as stronghold for that part of the work that cannot be otherwise verified because of the lack of data in the current literature. The experimental data in general seems to be the less precise, for different reasons. First for the internal discrepancies among the three studies quoted, and with the more recent study by Guilmot [46]. In addition to that ref. [41-43] are very old and substantial improvements could be made with more modern techniques.

Finally the results of our *ab initio* calculation can be plotted in an energy diagram for reaction (1) including the bonding and non bonding channels as shown in Fig. 2. As expected the two structural isomers having an atomic sequence HONO are more stable than the other possible tetra atomic combinations such as HOON or OONH that are far more unstable than the isomer having a central nitrogen atom. The complete details of the calculated bond length and bond angles of all species considered in this study and





Figure 2. The Energy diagram of the Potential Energy Surface of the NO + OH reaction scheme calculated with GAUSSIAN and plotted with CHEMDRAW [47] based on the output of the GAUSSIAN calculation.

Remarkably, according to our calculations the *cis* isomer seems to be slightly more stable than the *trans* one, probably because of some hydrogen bond like interaction between the hydrogen atom and the opposing oxygen. According to the preliminary calculations of this study the hydrogen is not shared between the two oxygen atoms though since such "sharing" configuration would require a higher energetic content. On the other hand the low energy barrier between the *cis* and the *trans* isomer seem to indicate a fast interconversion between these two structural isomers. Details on the calculated geometry of the reaction's products have not yet been fully explored and more theoretical work is needed to present a conclusive possible reaction's pathway for this reaction.

Species,	Energies, a.u.	<i>i</i>		B _i	<u>C</u>	artesian	coordinat	es,	v_{ir} cm ⁻¹
(point group)			a.u.	GHz		angs	stroms	-	-
н	E(B3LYP+ZPE)				Atom	Х	Y	Z	
	0.502155930011								
ΝΟ (C _{∞v})	E(B3LYP+ZPE)- 129.922172	A B C	0.00000 35.15744 35.15744	0.0000000 51.3331257 51.3331257	N O	0.0 0.0	0.0 0.0	-0.612 0.536	1989
HO (C∞v) ♪●	E(B3LYP+ZPE) -75.746087	A B C	0.00000 3.21989 3.21989	0.0000000 560.4975584 560.4975584	O H	0.0 0.0	0.0 0.0	0.108 -0.867	3705
NO + OH	E(B3LYP+ZPE) -205.66826 Erel = 0.0								
HNOO (C₅)	E(B3LYP+ZPE) -205.620607 Erel = 29.90209	A B C	20.26613 134.77669 155.04282	89.05211 13.39060 11.64028	N H O O	1.123 0.907 0.0 -1.096	-0.102 -1.119 0.466 -0.237	0.0 0.0 0.0 0.0	662, 943, 1081, 1311, 1532, 3234
cis-HONO (C _s)	E(B3LYP+ZPE) -205.74190 Erel = -46.20792	A B C	21.27843 136.01953 157.29796	84.81552 13.26825 11.47339	N O H	0.0 1.084 -1.014 -0.565	0.547 0.081 -0.401 -1.272	0.0 0.0 0.0 0.0	638, 718, 892, 1338, 1720, 3585
trans-HONO (C _s)	E(B3LYP+ZPE) -205.741469	A B	19.18850 143.83744	94.05329 12.54709	N O	0.0 -1.112	0.519 0.169	0.0 0.0	591, 619, 834, 1298, 1793, 3776

Table 2. In the following page B3LYP (with zero-point energy corrections (ZPE)) energies at 0 K, B3LYP/6-311G^{**} optimized Cartesian coordinates, unscaled vibrational frequencies (v_i), moments of inertia (I_i), and rotational constants (B_i) of all species involved in the NO+OH reaction mechanism. Molecular structures were drawn with CHEM 3 D [48] based on the output of Gaussian.

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Full Paper

	Erel = -45,93998	С	163.02594	11.07027	0	0.892	-0.602	0.0	
0					H	1.760	-0.174	0.0	
- (
TS HONO	E(B3LYP+ZPE)	А	21.70686	83.14150	Ν	0.236	0.509	0.042	671i, 558, 802, 1059, 1805,
(C ₁)	-205.72286	В	150.32025	12.00597	0	1.08	-0.280	0.0118	3758
	Erel = -34.26265	С	166.21717	10.85773	0	-1.116	-0.119	-0.122	
0 -6					Н	-1.365	-0.377	0.778	
TS H+ONO	E(B3LYP+ZPE)	A	24.26982	74.36155	Ν	0.0	0.575	0.0	1921i, 1029, 1243, 1302, 1400,
(C _s)	-205.697004	В	114.35836	15.78145	0	-1.000	-0.187	0.0	2097
	Erel = -18.03776	С	138.62818	13.01857	0	1.000	-0.187	0.0	
<u> </u>					Н	-0.001	-1.027	0.0	
U									
ONO	E(B3LYP+ZPE)	А	7.50385	240.50866	Ν	0.0	0.323	0.0	767, 1399, 1705
(C _s)	-205.626059	В	138.35432	13.04434	0	1.100	-0.141	0.0	
	Erel = 26.48090	С	145.85817	12.37326	0	-1.100	-0.141	0.0	

Table 3. Comparison between the calculated vibrational frequencies [cm⁻¹] reported in this work, [38], and [39] and the experimental data available for this system.

	This work	[38]	[39]	Exp. [41-43]
n ₁	519.0	596.0	600.9	540
n ₂	619.0	631.1	-	593
n ₃	834.0	862.2	796.0	791
n ₄	1298.0	1305.9	1267.6	1265
n ₅	1793.0	1791.8	1690.0	1699
n ₆	3776.0	3756.8	3591.0	3588

Table 4. Bonu lei	igth [A] and bo	nu angle [degrees] o	calculated in th	is study
Species	Bond	Length [Å]	Bond	Angle [degree]
ОН	OH	0.98		
NO	NO	1.15		
HNOO	HO	1.04	NOO	120.5
	NO	1.26	HNO	104.8
	00	1.3		
cis-HONO	HO	0.98	ONO	113.7
	ON	1.18	HON	105.8
	NO	1.39		
trans-HONO	HO	0.97	ONO	111
	ON	1.17	HON	102.3
	NO	1.43		
TS HONO	HO	0.97	ONO	111.6
	ON	1.16	HON	109.5
	NO	1.5		
TS H+ONO	NO	1.26	ONO	105.4
	NO	1.26	HNO	7.3
	HO	1.31		
ONO	NO	1.19	ONO	134.2
	NO	1.19		

Full Paper

 Table 4. Bond length [Å] and bond angle [degrees] calculated in this study

In addition to that while this study bring some light in uncovering the energetic pathway for the formation of HONO from the reaction of the hydroxyl radical and nitric oxide in gas phase more work is needed in terms of experimental product yield determination to confirm the conclusion of this study and to eventually infer possible atmospheric implications.

Conclusion

The kinetic of formation of nitrous acid (HONO) has been previously investigated, and literature indicates a general agreement on the overall rate of reaction under atmospheric conditions [12] the kinetic constant four reaction (1) being in the range of $k=6*10^{-12}$ [cm³ molecule⁻¹ s⁻¹] under tropospheric pressure at room temperature. Complementing ref. [12] the present work presents a detailed *ab intio* study focused on the allowed reaction's pathways for the HONO formation from OH and NO and of the geometry of the resulting products confirming that the main product for this reaction is HONO. From the theoretical point of view the most recent studies published so far on the HONO system are the ones by Richter, et al. [41-42], and the ones by Bauerfeldt and its group [40] but, for the purpose of this work, they lack of focus in terms of analyzing possible atmospheric implication for the title reaction although they serve to support indirectly the conclusions of the present work.

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