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Overtone-Induced Reactions on the HO_2NO_2 Potential Surface

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We report density-functional theory calculations performed at the B3LYP/6-311++G(3df,3pd) level on the lowest energy singlet and triplet potential energy surfaces of the HO_2NO_2 system. The reaction forming HONO + ground-state oxygen, O_2 ($^3\Sigma$), from $HO_2 + NO_2$ proceeds via a triplet transition state which lies about 2 kcal/mol above reagents, and about 22 kcal/mol above ground-state HO_2NO_2. Dissociation of ground-state pernitric acid into $HO_2 + NO_2$ is energetically accessible through excitation of the $\upsilon = 2$ overtone level of the OH stretching vibration ($v_{OH} = 2$). Overtone excitation into $v_{OH} \geq 3$, followed by a singlet−triplet potential surface crossing, could lead to HONO + O_2 ($^3\Sigma$) products. On the singlet potential surface, the energetic barrier to the reaction forming HONO + O_2 ($^1\Sigma$) lies very near the product energy. This product channel may be accessible via excitation of the $v_{OH} = 3$ or 4 overtones. Complexation with a single water molecule does not alter the barrier height to reaction, but may promote reaction by changing the strength and or location of the singlet−triplet coupling. The reaction of HONO ($v_{OH} \geq 3$) with O_2 ($^3\Sigma$) may form $HO_2 + NO_2$ in polluted urban atmospheres with a rate several orders of magnitude smaller than that of HONO photolysis.

Introduction

The odd-hydrogen (HO_x) and odd nitrogen (NO_x) cycles are strongly coupled in the atmosphere. Understanding the chemical reactions responsible for this coupling is of great importance because both cycles have a great influence on ozone concentration. Recently, the reactions of OH + NO_2,[1] OH + HNO_3,[2,3] OH + HONO,[4] and HO_2 + NO_2[5] have received both experimental and theoretical scrutiny.

Nitrous acid, HONO, is an important source of OH at sunrise, via its near-UV photolysis: HONO + $h\nu \rightarrow$ OH + NO in the wavelength range 320−400 nm.[6] In polluted atmospheres, the early-morning production of OH by HONO photolysis is the dominant source of hydroxyl; under some conditions, it may produce more OH over the day than formaldehyde photolysis or reactions of O(^{1}D) produced by ozone photolysis. Despite its importance, the atmospheric production of HONO is not well understood, either in the troposphere or the lower stratosphere. Heterogeneous reactions are believed to play an important role in its formation.

The production of HONO from the reaction of $HO_2 + NO_2$ has been postulated for some time. First proposed in the mid-1970s to account for product distributions in HO_2−NO_2−NO reaction mixtures,[7,8] it is currently believed to occur only very slowly, if at all. Tyndall et al.[9] in 1995 established an upper limit of 5×10^{-16} cm^3 molec^{-1} s^{-1} for the room-temperature rate coefficient. Very recently, Dransfield et al.[10] failed to observe any HONO formation from the reaction, and concluded that the exclusive fate (apart from dissociation to reagents) is production of HO_2NO_2. This finding suggests either that the barrier to the reaction lies at an energy inaccessible to room-temperature reagents, or that there is a very unfavorable preexponential term, due to a highly constrained transition state geometry, for instance.

Recently, Donaldson et al.[11,12] have proposed that the overtone-induced dissociation of molecules such as HO_2NO_2 following absorption of solar radiation into overtones of the OH stretching vibration might play a significant role in HO_x production during sunrise and sunset. Overtone pumping of the OH local modes deposits significant amounts of energy into the molecule in a highly nonthermal manner. Rapid intramolecular vibrational redistribution (IVR) gives rise to migration of energy out of the OH stretch and into other types of internal motion of the molecule. Of particular interest in our previous work has been the migration of sufficient energy into the weakest bonds to cause their rupture, releasing HO_x and NO_x. The dissociation of nitric acid[13] and H_2O_2[14] is known to occur rapidly, with almost unit quantum efficiency, upon excitation of OH stretch levels lying above the energetic dissociation limit. Measurements and calculations of the absolute absorption cross section and frequencies of the OH overtone vibrations in nitric[15] and pernitric[16,17] acids have been reported, confirming the potential importance of the overtone-induced dissociation mechanism. Very recent work by Wennberg and co-workers[18] has demonstrated this experimentally: HO_2 is measured as a product following the photoexcitation of the OH overtone vibrations $v_{OH} \geq 2$ of HO_2NO_2. The HO_2 yield increases with increasing temperature, suggesting that the dissociation threshold lies close to the $v_{OH} = 2$ energy.

As well as a simple bond cleavage, a molecular rearrangement−dissociation channel may be accessed by vibrationally excited HO_2NO_2. Ravishankara[19] has suggested the possibility

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of an overtone-induced (or aided) hydrogen-atom migration, followed by dissociation to HONO + O_2. This reaction mechanism has not previously been considered, and may indeed play a more general role in the atmosphere. Another previously unconsidered possibility is the reaction of overtone-excited molecules with O_2, producing HO_2. In particular, the reaction of vibrationally excited HONO with ambient O_2 could play a role in its atmospheric chemistry.

The object of this paper is to explore features of the singlet and triplet potential energy surfaces of the HO_2NO_2 system, with the aim of establishing barrier heights and transition state geometries for: (a) dissociation of HO_2NO_2 to HO_2 + NO_2; (b) isomerization-dissociation of HO_2NO_2 to give HONO + O_2; (c) reaction of HONO + O_2 to give HO_2 + NO_2. The significance of these processes to the atmospheric chemistry of HONO is estimated, using known or estimated overtone absorption cross sections. As a secondary issue, the possibility of lowering barrier(s) to reaction by clustering with water was also explored.

Calculations

All calculations were carried out using the GAUSSIAN 98[20] suite of programs and basis sets. The geometries of all species considered were optimized using density functional theory with the B3LYP functional.[21] Calculations were initially performed using the 6-31+G** basis set. Geometries were then re-optimized, with the 6-311++G(3df,3dp) basis. The optimized geometries of bound species were determined to be true minima by the absence of imaginary frequencies in the calculated vibrational spectrum; those of transition states were identified by their single imaginary frequency. Transition state structures were located using the Synchronous Transit-Guided Quasi-Newton method,[22] as implemented by the GAUSSIAN 98 package. In this approach, an intitial guess for the transition state structure is automatically generated by the program, given optimized reagent and product geometries as input. A full geometry optimization is then performed on this guess, resulting in an optimized transition state geometry. In the present calculation, the input geometries were fully optimized reactant minima (the pernitric acid ground state for the singlet; a weakly bound HO_2-NO_2 complex in the case of the triplet) and weakly bound singlet and triplet HONO$-O_2$ complexes for the products. Zero-point energies were obtained from the harmonic frequencies calculated at the B3LYP/6-311++G(3df,3dp) level without correction; we take these to represent an upper limit to the true values. Our previous work on the complexes of HO_2NO_2, HNO_3, and HONO with water has indicated that basis set superposition energy (BSSE) is negligible at the present level of calculation for the species considered here.[23]

Results and Discussion

Table 1 presents the electronic and zero-point energies calculated at the B3LYP/6-311++G(3df,3dp) level for the stationary points of interest here. The calculated energetics for various reactive channels are given in Table 2, with and without the zero-point correction. Where available, experimental energetics are shown as well, for comparison.[24] Overall, the agreement with experiment is quite good, with the energetics calculated without the zero-point correction showing excellent agreement with experiment. The zero-point corrected calculations consistently underestimate the energy differences in endoergic processes and overestimate those for exoergic processes, with respect to experimental values. In the following, energies are reported without the zero-point correction, unless otherwise indicated.

TABLE 1: Energies and Zero-point Corrections at the B3LYP/6-311++G(3df,3dp) Level

species	energy (hartree)	zero-point correction (hartree)
HO	−75.766245	0.008461
HO_2	−150.968332	0.014150
NO_2	−205.155297	0.008803
NO_3	−280.3290338	0.010561
HO_2NO_2	−356.157357	0.029211
$^3HO_2NO_2$	−356.103204	0.025127
HONO	−205.786522	0.020224
O_2 ($^1\Sigma$)	−150.317943	0.003714
O_2($^3\Sigma$)	−150.379284	0.003739
^{3}TS	−356.120550	0.021802
^{1}TS	−356.107412	0.024904

TABLE 2: Reaction Energies[a]

reaction	ΔE	ΔE(zpc)	ΔH(exp)[b]
OH + NO_3 → HO_2NO_2	38.9	32.5	38.8
HO_2 + NO_2 → HO_2NO_2	21.2	17.2	20.9
HO_2NO_2 → HONO + O_2($^3\Sigma$)	−5.3	−8.6	−5.8
HO_2NO_2 → HONO + O_2($^1\Sigma$)	33.1	29.9	31.9
HO_2NO_2 → $^3HO_2NO_2$ (adiabatic)	18.2	15.6	
HO_2NO_2 → ^{3}TS	23.1	18.4	
HO_2NO_2 → ^{1}TS	31.3	28.6	

[a] Energies in kcal/mol. [b] From ref 24.

Figure 1 displays the calculated energetic pathways listed in Table 2. Because agreement with experiment is best when the zero-point energies are not included, the uncorrected energies are illustrated here. The lowest energy potential surface is the singlet ground state of pernitric acid, which correlates to two channels giving ground-state products: HO_2 + NO_2 and OH + NO_3, and one channel yielding excited-state oxygen mol-

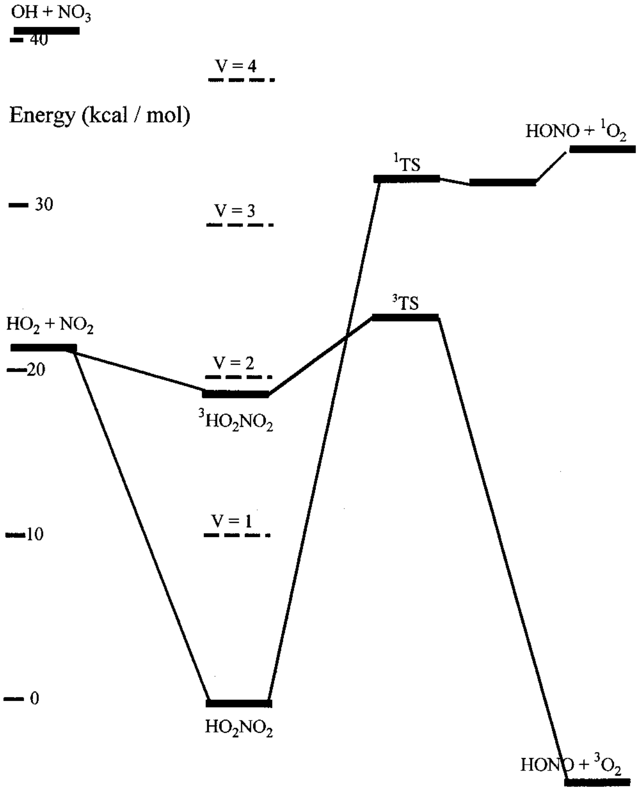

Figure 1. Schematic of the low energy reaction pathways for dissociation of pernitric acid. The dashed lines represent the energies of various levels of the OH stretching vibration in pernitric acid.

ecules: HONO + $O_2(^1\Sigma)$. The singlet channel yielding OH and that giving $O_2(^1\Sigma)$ lie fairly close in energy; the HO_2-producing channel lies considerably lower. There are also triplet potential energy surfaces which correlate to all three dissociation channels. The lowest of these corresponds to the "direct" reaction in which NO_2 abstracts a hydrogen from HO_2 on the triplet surface; it connects $HO_2 + NO_2$ to HONO + $O_2(^3\Sigma)$ via a weakly bound complex and a low activation barrier.

(a) Dissociation to $HO_2 + NO_2$. The energies of the OH stretching vibrational mode of HO_2NO_2, calculated from the parameters given in Fono et al.[16] are also illustrated in Figure 1. The energy of the $v_{OH} = 2$ level lies only 1.4 kcal/mol below the calculated (and experimental) energy of $HO_2 + NO_2$. This is coincidentally the same energy gap that exists between the $v_{OH} = 5$ OH stretching overtone of nitric acids and the OH + NO_2 product channel in that molecule. In that case, dissociation is observed, promoted by internal (particularly, rotational) energy in the nitric acid molecule.[13] We anticipate similar behavior here, and so conclude that excitation of the $v_{OH} = 2$ vibration will cause dissociation of HO_2NO_2, and that the dissociation yield will be a strong function of temperature.

Our previous work has concentrated on the increase in the pernitric acid photolysis rate due to overtone-induced dissociation of HO_2NO_2 from $v_{OH} \geq 3$.[11,12] HO_x production from this source explains the observed zenith angle dependence of lower stratospheric HO_x production at dawn, but does not quantitatively reproduce the measured concentrations.[25] Recent experiments of Wennberg and co-workers,[18] as well as the present calculation, indicate that dissociation from $v_{OH} = 2$ is also possible. Because the oscillator strength for absorption into $v_{OH} = 2$ is expected to be approximately 10 times greater than that for absorption into $v_{OH} = 3$,[15,17] inclusion of dissociation from $v_{OH} = 2$ could possibly bring measured and calculated lower stratospheric HO_x production at dawn and dusk into quantitative agreement.

The calculated dissociation threshold lies approximately 1.5 kcal/mol above the rotationless $v_{OH} = 2$ energy. At 220 K, the temperature of the middle stratosphere, about 5% of a population of pernitric acid molecules contain this amount of rotational energy. The fraction grows to approximately 8% at room temperature. We estimate the contribution to the total dissociation rate from overtone excitation to $v_{OH} = 2$ to be about 50% of that from the $v_{OH} = 3$ level at 220 K, and about equal to that from $v_{OH} = 3$ at room temperature, assuming equal photon fluxes at the wavelengths corresponding to absorption. We conclude that dissociation from $v_{OH} = 2$ should be included in atmospheric chemistry models and that this process will make a significant contribution to the calculated lower stratospheric HO_x production rates at high solar zenith angles.

(b) Reactions Forming O_2 + HONO. Figure 2 shows the calculated lowest energy reaction path on the triplet surface, which involves a simple hydrogen transfer between reagents. A complex formed between the reagents is bound by about 3 kcal/mol and is illustrated in Figure 2a. Figure 2b displays the geometry of the triplet transition state and Figure 2c shows the ground state (triplet) products. The geometry and harmonic vibrational frequencies of this transition state are reported in Tables 3 and 4, respectively. The barrier to the direct reaction on the triplet surface is about 2 kcal/mol; the calculated reaction exoergicity is 26.5 kcal/mol, in excellent agreement with experiment.[24]

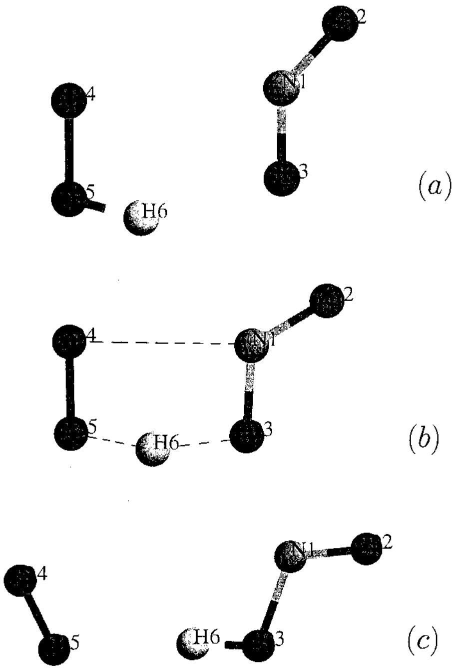

Figure 2. Minimum energy pathway for the direct abstraction of hydrogen from HO_2 by NO_2 on the triplet potential energy surface. (a) HO_2-NO_2 complex; (b) triplet transition state; (c) HONO + $O_2(^3\Sigma)$ products.

TABLE 3: Geometry of Triplet Transition State

bond	bond length (Å)	angle	
N_1-O_2	1.19	$O_2-N_1-O_3$	124.21^0
N_1-O_3	1.27	$N_1-O_3-H_6$	100.08^0
O_3-H_6	1.31	$H_6-O_5-O_4$	103.5^0
H_6-O_5	1.13		
O_4-O_5	1.28		
N_1-O_4	2.51		

TABLE 4: Harmonic Frequencies of Triplet Transition State

mode no.	frequency (cm^{-1})	IR intensity (km/mol)
1	−1284.3048	1023.0252
2	149.8752	1.3789
3	156.0678	0.8811
4	165.8458	2.7158
5	365.3111	0.3721
6	667.4691	33.5657
7	828.0312	69.7079
8	1097.5817	103.4859
9	1321.4177	132.8301
10	1363.3036	211.6281
11	1652.4832	551.4362
12	1802.4990	62.1590

In the experiments reported by Dransfield et al.[10] no evidence for HONO formation was found, leading those authors to conclude that the barrier to reaction is higher than the reagent energy available in that experiment. Our results suggest that the barrier on the triplet surface lies at a relative energy which is accessible to room-temperature $HO_2 + NO_2$ reagents. From a strictly statistical standpoint, one would expect most of the reactive flux to proceed on the triplet surface; the lack of HONO formation is puzzling in this regard. However, in cases where there is, in addition to a direct reactive channel, also a strongly bound intermediate accessible to reagents, very often most or all of the trajectories access this route. For example, the reaction of $O(^3P)$ with vinyl radical, C_2H_3,[26] is thought to proceed exclusively via formation of the vinoxy radical, followed by H-atom migration to form CO + CH_3. No evidence for OH formation (an exoergic process) is observed. Similarly, the reactions of F-atoms with C_2H_3[27] and with HCO[28] yielding HF both proceed exclusively via formation of a highly excited, strongly bound intermediate molecule, rather than by a direct abstraction over a very low energy barrier. We propose that similar dynamics hold in the present case: effectively, all of the trajectories of the approaching reagents end up on the singlet surface, and explore phase space of the highly energized pernitric acid molecule, rather than proceeding on the triplet surface directly to products. Formation of ground-state pernitric acid, as reported by Dransfield et al.,[10] is consistent with this picture. The lack of HONO production may be a consequence of the singlet−triplet crossing seam being inaccessible at the energy available to the reagents.

On the other hand, the reaction of OH with NO_3 is predicted to possess sufficient energy for reaction to take place entirely on the ground-state singlet potential energy surface, forming HONO + $O_2(^1\Sigma)$. To our knowledge, this reaction has not been investigated experimentally.

From a strictly thermochemical standpoint, the dissociation of ground-state pernitric acid to HONO + $O_2(^3\Sigma)$ is somewhat exoergic, by about 5 kcal/mol. There must therefore exist a singlet−triplet surface crossing somewhere along the potential surface connecting ground-state HO_2NO_2 to ground-state products, HONO + $O_2(^3\Sigma)$. This crossing is not necessarily along the minimum energy path, but if it is accessible to the reactive system, the channel forming HONO and ground-state oxygen may be accessed by excited singlet pernitric acid.

To our knowledge, there is no report of the unimolecular dissociation of HO_2NO_2 yielding HONO + O_2 as products. Thermal dissociation is reported to occur exclusively via simple bond cleavage yielding HO_2 + NO_2 as products. An average of the preferred low pressure and high-pressure rate coefficients for this reaction[29] suggest an activation barrier of 21.7 kcal/mol, about 1 kcal/mol above the reported enthalpy change for this process. Because thermal unimolecular reactions typically follow the lowest energy pathway to products, these data suggest that the effective barrier to HONO + $O_2(^3\Sigma)$ production must lie higher in energy than the HO_2 + NO_2 product channel.

OH overtone excitation represents a process which could produce sufficiently excited HO_2NO_2. Because overtone pumping initially deposits energy into the OH stretching motion, the possibility exists that H-atom migration could be facilitated, promoting intramolecular rearrangement and ultimately, HONO formation. The calculated energies illustrated in Figure 1 indicate that from a strictly energetic point of view, excitation of $v_{OH} = 2$ of the OH stretch would provide sufficient energy to overcome the barrier on the triplet potential surface, if the singlet−triplet surface crossing seam is at a similar or lower energy. It seems more likely, given the experimental results, that the crossing seam is higher in energy than the barrier. If so, then the excitation of $v_{OH} = 3$ or $v_{OH} = 4$ might be sufficient to access the crossing seam and give ground-state HONO + O_2 products.

Reaction on the singlet potential surface should be more straightforward. Figure 3 shows the calculated minimum energy pathway for dissociation on the singlet surface, forming HONO + $O_2(^1\Sigma)$. Intramolecular migration of hydrogen occurs via a five-membered ring structure; the transition state lies about 31 kcal/mol above the ground state, very close in energy and geometry to the singlet products. Its geometry and harmonic vibrational frequencies are reported in Tables 5 and 6, respectively. Clearly, depositing energy into O−H motion should help to promote this migration. Excitation of $v_{OH} = 3$ is predicted to provide roughly sufficient energy for the dissociation to occur on the singlet surface. Certainly, excitation of $v_{OH} = 4$ will provide sufficient energy for dissociation, which could then be rapid (on the ps time scale). We suggest that this process might be occurring in competition with the OH and HO_2 formation channels, following excitation of the $v_{OH} = 3$ or $v_{OH} = 4$ overtones.

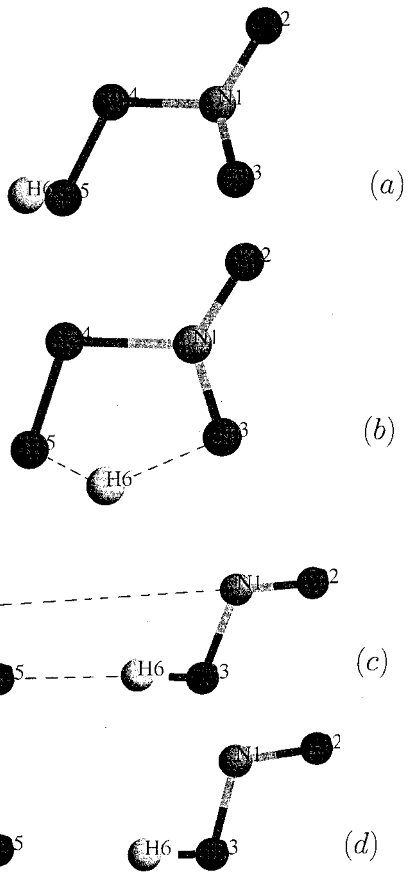

Figure 3. Minimum energy pathway for the intramolecular hydrogen transfer on the singlet potential energy surface. (a) ground-state pernitric acid; (b) hydrogen migration; (c) singlet transition state; (d) HONO + $O_2(^1\Sigma)$.

TABLE 5: Geometry of Singlet Transition State

bond	bond length (Å)	angle	
N_1-O_2	1.18	$O_2-N_1-O_3$	111.16^0
N_1-O_3	1.42	$N_1-O_3-H_6$	103.31^0
O_3-H_6	0.98	$H_6-O_5-O_4$	114.36^0
H_6-O_5	2.11		
O_4-O_4	1.21		
N_1-O_4	4.02		

TABLE 6: Harmonic Frequencies of Singlet Transition State

mode no.	frequency (cm^{-1})	IR intensity (km/mol)
1	−26.7064	2.3056
2	32.5056	1.1125
3	76.3079	10.1045
4	102.2176	2.6841
5	133.4345	1.3727
6	644.5133	114.1195
7	649.4335	98.5736
8	851.1635	189.6789
9	1343.2067	178.6833
10	1631.2027	0.1099
11	1771.3188	182.8283
12	3669.6983	371.9123

If we assume that all of the molecules excited into the $v_{OH} = 3$ or $v_{OH} = 4$ levels isomerize and dissociate, either on the triplet or singlet surface, the upper limit to the production rate

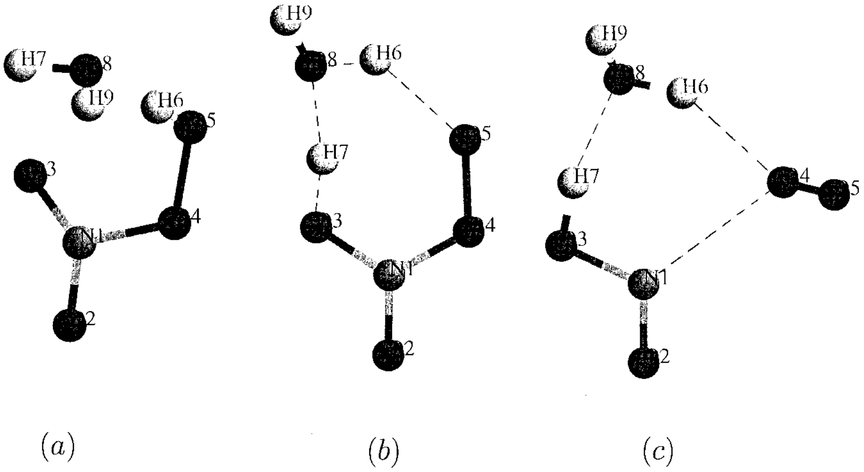

Figure 4. Similar to Figure 3, but for the water-catalyzed reaction on the singlet surface. (a) reactants; (b) transition state; and (c) products.

of HONO may be estimated from the measured absorption cross sections for the $v_{OH} = 3$ transition[16,17] and solar fluxes near 1000 nm.[30] We calculate this upper limit to be on the order of $10^{-6}[HO_2NO_2]$ molec cm^{-3} s^{-1}. With a 20 km mixing ratio of 2×10^{-10} for HO_2NO_2,[31] this amounts to a maximum value for the "extra" HONO production rate of 10^2-10^3 molec cm^{-3} s^{-1}. This value is probably too small to affect ozone chemistry in the stratosphere.

(c) Reaction of O_2 ($^3\Sigma$) + HONO (v). The abstraction of hydrogen from HONO by ground-state oxygen molecules is just the reverse of the reaction of HO_2 with NO_2, and so is endoergic by 26.5 kcal/mol at the B3LYP/6-311++G(3df,3dp) level, with a predicted barrier of 28.4 kcal/mol. The geometry of the triplet transition state shown in Figure 2 suggests that vibrational excitation of the OH stretch of HONO might be effective in surmounting the activation barrier. The overtone spectrum of HONO has been measured, using vibrationally mediated dissociation of HONO and observation of the OH product.[32] The $v_{OH} = 3$ absorption in HONO is centered around 975 nm, corresponding to an energy of about 29 kcal mol^{-1}. We therefore expect that ground-state O_2 could abstract hydrogen from HONO excited to $v_{OH} \geq 3$. Endoergic hydrogen transfer reactions of this type, with "late" barriers (i.e., in which the transition state resembles the products) are often aided by vibrational excitation,[33] with rate coefficients increasing by many orders of magnitude.[34] It would not be unreasonable to expect a similar enhancement in the rate coefficient here, as well.

To determine the potential importance of this process to HO_x production in the atmosphere, we estimate the steady-state concentration of HONO ($v_{OH} = 3$) and its reaction rate with O_2, and compare the resulting "extra" HO_x production rate to that due to HONO photolysis in the near-ultraviolet region. Assuming the absorption coefficient to $v_{OH} = 3$ in HONO is similar to that in nitric acid[15] and that every collision of excited HONO with O_2 gives rise to reaction, the upper limit of the HO_2 production rate by this mechanism is approximately 10^4 molec cm^{-3} s^{-1}, for a HONO mixing ratio of 1 ppb in the lower troposphere. This is several orders of magnitude smaller than the OH production rate by near UV photolysis of HONO under these conditions, which is about 1.5×10^8 molec cm^{-3} s^{-1}.[6] However, even though the HO_x production is not significantly affected, this process forms NO_2 rather than NO, and so has the potential to alter the ozone formation chemistry in polluted atmospheres.

(d) Reaction of the Water Clustered Species. Although there is no experimental evidence that HONO is formed from HO_2NO_2 reactions in the gas phase, there has been a suggestion that the decomposition to form HONO does occur heterogeneously.[35] Several atmospherically important reactions are known to require the presence of catalysts: the hydrolysis of $ClONO_2$[36] and SO_3[37] are both catalyzed by the possibility formation of cyclic transition state species with water. Simple inspection suggests that a cyclic water complex with HO_2NO_2 might catalyze HONO production as well.

TABLE 7: Reaction Energies for Water-complex Reaction[a]

reaction	ΔE	ΔE(zpc)
$HO_2NO_2\ (H_2O) \rightarrow HONO\ (H_2O) + O_2(^3\Sigma)$	−4.5	−7.1
$HO_2NO_2\ (H_2O) \rightarrow HONO(H_2O) + O_2(^1\Sigma)$	31.2	29.5
$HO_2NO_2\ (H_2O) \rightarrow {}^3TS\ (H_2O)$	26.2	21.8
$HO_2NO_2\ (H_2O) \rightarrow {}^1TS\ (H_2O)$	33.3	32.1

[a] Energies in kcal/mol.

We have previously reported the geometries and binding energies for the complexes of pernitric acid and HONO with water.[23] The hydrogen bonded interaction is quite strong, with the acid acting as the hydrogen donor and the water as the acceptor in both cases. Li et al.[38] have measured a very high uptake coefficient for pernitric acid exposed to water ice at 193 K, consistent with this strong binding. Figure 4 displays the reaction pathway we calculate on the singlet surface for the reaction

$$HO_2NO_2 - H_2O \rightarrow HONO - H_2O + O_2$$

The water molecule acts as a catalyst to reaction, transferring a hydrogen (H7 in the Figure) to the NO_2 moiety, and accepting one (H6) from the HO_2 moiety. The energetics we calculate for this process are reported in Table 7, as well as those for the corresponding reaction on the triplet potential surface. Surprisingly, there is no decrease in the energetic barrier in the reaction involving the water complex, on either the triplet or the singlet potential energy surface. Our previous work[23] indicates that binding to water does not change the relative overall energetics of the bond cleavage reactions, giving OH− or HO_2- products, either. In the experiments of Li et al.,[38] when the ice was warmed above 225 K, the adsorbed pernitric acid started to desorb as HNO_4. No evidence is reported in that work for the production of HONO by adsorbed pernitric acid, consistent with our finding that the energetics for this process do not change due to binding of a water molecule.

Although this result is surprising at first, it may be explained on the basis of the strength and nature of the binding of water to the acids. In both acids, very strong hydrogen bonds are formed with water. Because the nature of the binding at the transition state is similar to that in pernitric and nitrous acids, the transition state is stablized by roughly the same amount as the reagents and products, resulting in little change in the barrier height to reaction. It may be that inclusion of more water molecules in the calculation, to better mimic a "surface" might lower the barrier.

Alternatively, it might be the case that the presence of a surface catalyses the reaction by bringing the singlet–triplet crossing region into a region accessible to thermal reagents. The electric and magnetic fields associated with molecules can be strong enough to perturb the electronic states of nearby molecules, such as any partners involved in a complex, or in solution.[39] The effects of complex formation on optical transition probabilities and photochemistry of atmospheric gases have been outlined recently by Vaida, Naaman, and co-workers.[40] For example, the presence of water in the ozone-water complex is though to give rise to a very large enhancement[41] (reported to be at least a factor of 100) of the spin-forbidden dissociation of ozone into $O(^1D) + O_2\ (^3\Sigma)$.

Conclusions

The important stationary points (transition states and minima) on the singlet and triplet potential surfaces for the reaction system

$$HO_2 + NO_2 \rightarrow HO_2NO_2 \rightarrow HONO + O_2$$

have been calculated at the B3LYP/6-311++G(3df,3dp) level. Several points have been inferred from the results:

1. The barrier for HONO formation on the triplet surface lies slightly above the energy of $HO_2 + NO_2$ and close to the energy of $v = 2$ of the OH stretch of ground-state HO_2NO_2. Because no HONO production is observed from the $HO_2 + NO_2$ reaction, there may be other features which control the dynamics. We suggest that reactive trajectories all form ground state (singlet) pernitric acid, and that the singlet–triplet crossing region is not easily accessible at these energies;

2. HO_2NO_2 is predicted to dissociate into $HO_2 + NO_2$ following absorption of near-IR radiation into its $v_{OH} = 2$ overtone mode. This prediction is consistent with recent experimental work;[18]

3. A rearrangement channel of excited HO_2NO_2, forming $HONO + O_2$ (either singlet or triplet) is possible following excitation of the $v_{OH} \geq 3$ overtone mode;

4. The reaction of vibrationally excited HONO (with $v_{OH} \geq 3$) with O_2 could occur quite efficiently;

5. Complexation of pernitric acid with water does not lower the barrier to HONO production.

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