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Thermochemical Properties of H_xNO Molecules and Ions from ab Initio Electronic Structure Theory

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Coupled-cluster calculations through noniterative triple excitations were used to compute optimized structures, atomization energies at 0 K, and heats of formation at 0 and 298 K for NH_2O, HNOH, NH_2O^-, NH_2OH^+, NH_3OH^+, HNO^-, and HON. These molecules are important in the gas-phase oxidation of NH_3, as well as its solution-phase chemistry. The O−H, N−H, and N−O bond energies of these molecules are given and compared. The N−H and O−H bond energies are quite low, and, for NH_2OH, the O−H bond is weaker than the N−H bond (by 7.5 kcal/mol). The energetics for a variety of ionic chemical processes in the gas phase, including the electron affinities of NH_2O and HNO, the proton affinities of NH_2O and NH_2OH, and the acidities of NH_2OH and NH_2O, are given. The compounds are weak bases and weak acids in the gas phase. Solvation effects were included at the PCM and COSMO levels. The COSMO model gave better values than the PCM model. The relative values for pK_a for NH_2O and NH_2OH are in good agreement with the experimental values, showing both compounds to be very strong bases in aqueous solution with NH_2OH being the stronger base by 1.8 p*K* units at the COSMO level, compared to the experimental p*K* difference of 1.1 ± 0.3 p*K* units. We predict that NH_2OH^+ will not be formed in aqueous solution, because it is a very strong acid. Based on the known acidity of NH_3OH^+, we predict $pK_a(NH_2OH^+) = -5.4$ at the COSMO level, which is in good agreement with the experimental estimate of $pK_a(NH_2OH^+) = -7 \pm 2$.

Introduction

The gas-phase oxidation of ammonia (NH_3) in the atmosphere is considered to be one of the major sources of NO_x, along with sources from fossil fuel and biomass burning.[1,2] Early atmospheric oxidation studies of NH_3 found that, after the initial reaction of OH radicals with NH_3, the resulting byproduct of the oxidation is HNO.[3] Dentener and Crutzen[4] and later Kohlmann and Poppe[5] used atmospheric modeling studies to show that the oxidation of NH_3 could lead to a significant production of N_2O. However, there were considerable uncertainties in these estimates, largely because of an incomplete understanding of the gas-phase oxidation mechanism. All of the oxidation intermediates involved in the gas-phase oxidation mechanism of NH_3 have not been fully characterized, including their impact on atmospheric chemistry. For example, in the oxidation of NH_3, the NH_2 radical is produced. This radical can react with O_2 to give the amineperoxy NH_2O_2 radical, which is unstable, but this reaction is ignored in some atmospheric models.[4] The self-reaction of the NH_2O_2 radical or with other species can result in the formation of NH_2O, which is an important intermediate that can help to account for the formation of HNO in the oxidation of NH_3. However, this reaction is also ignored in most atmospheric models, and, instead, the reaction of NH_2 radicals with ozone is most often used to account for the formation of NH_2O. It is not clear from the atmospheric model studies whether NH_2O or its isomer HNOH is involved in the subsequent oxidation chemistry. Kohlmann and Poppe[4] have shown that the formation of the isomer HNOH could have a major influence on the subsequent production of atmospheric N_2O and NO_x. They also note that many crude chemical reaction schemes have been used to model the atmospheric impact of NH_3 and its influence on the NO_x budget.

Given the major uncertainties in the gas-phase oxidation chemistry of NH_3, the aqueous-phase oxidation chemistry is even more uncertain. Despite the fact that NH_3 has an important role in the neutralization of acidic aerosols and acid rainwater droplets,[6] little is known about the solution-phase thermodynamics of some of the key oxidized species. There is substantial current interest in developing an understanding of the biochemical mechanism for the bacterial oxidation of NH_3.[7] An important intermediate in the oxidation scheme is hydroxylamine (NH_2-OH), which has interesting chemical properties, in that it can be both oxidized and reduced. Reduction leads to the formation of NH_3, and oxidation leads to the formation of nitrogen oxides. Central to understanding the chemistry in aqueous solution, and, thus, the biological processing of ammonia and hydroxylamine, is an understanding of the aqueous oxidation chemistry of

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NH_2O, which is a key intermediate that results from the aqueous one-electron oxidation process.[8−10]

H_2NO or its isomer HNOH is considered to be a key intermediate during the aqueous one-electron oxidation of hydroxylamine (H_2NOH). Hydration could favor the HNOH isomer, and it has been suggested to be the most stable intermediate in solution.[11,12] This conclusion is based on the finding that the one-electron oxidized (the oxidant being OH) forms of both H_2NOH and H_2NOCH_3 seem to have pK_a values ca. 2 pH units below those of the parent compound. However, given that the protonated parents H_3NOH^+ and $H_3NOCH_3^+$ have negligible reactivities toward OH, this could be a kinetic artifact (i.e., the apparent pK_a observed could be the pH at which the effective rate of OH reacting solely with the remaining fraction neutral parent becomes equal to the rate of radical recombination to yield products). Hung et al.[10] cited evidence from the literature based mainly on electron paramagnetic resonance (EPR) measurements that seems to indicate H_2NO is the most stable form. Stable alkyl nitroxyl radicals (e.g., TEMPO (2,2′, 6,6′, tetramethyl piperidinoxyl) radicals) are known and widely used as spin traps and redox catalysts in chemical and biochemical systems. For example, EPR studies of nitroxyl radicals such as TEMPO have shown that the radical can only be protonated at oxygen in concentrated solutions of H_2SO_4.[13]

In both the gas-phase and aqueous-phase oxidation chemistry of NH_3, the subsequent chemical fate of the NH_2O radical is the major uncertainty. This seems paradoxical, because the NH_2O radical, which is the simplest nitroxide radical, has been studied theoretically for many years.[14−17] There is considerable controversy regarding whether the planar structure or nonplanar structure is the true minimum. Mikami et al.[18] suggested that the molecule is planar, based on the hyperfine structure in the microwave spectrum. At the CISD/cc-pVDZ level, Soto et al.[16] found the nonplanar structure to be lower in energy that the C_{2v} planar structure. Komaromi and Tronchet[17] calculated the structure of NH_2O with several different basis sets and levels of correlation and predict that the molecule is almost planar with a negligible inversion barrier. Soto et al.[16] calculated the heat of formation of NH_2O at the CISD level with an extended cc-pVTZ basis set and obtained a value of 17.9 kcal/mol at 0 K and 16.2 kcal/mol at 298 K. Soto et al. predicted HNOH to be less stable than NH_2O, by 5.8 kcal/mol. However, it has been postulated that HNOH is more stable in aqueous media, because hydration has been predicted to shift the order of stability. If this is, indeed, the case, there are important consequences for chemical mechanisms for the aqueous oxidation, and this may explain differences between the gas-phase chemistry and aqueous chemistry of NH_3.

To understand the mechanism and product yield of recombination, reliable thermodynamic data are needed. We have been developing an approach[19−25] to the reliable calculation of molecular thermodynamic properties—notably, heats of formation—based on ab initio molecular orbital theory. Our approach is based on calculating the total atomization energy of a molecule and using this with known heats of formation of the atoms to calculate the heat of formation at 0 K. This approach starts with coupled-cluster theory, including a perturbative triples correction (CCSD(T)),[26−28] combined with the correlation-consistent basis sets[29,30] extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by several smaller additive corrections, including core-valence interactions and relativistic effects, both scalar and spin−orbit. Finally, one must include the zero-point energy (ZPE) obtained either from experiment, theory, or some combination. The standard heats of formation of compounds at 298 K can then be calculated, using standard thermodynamic and statistical mechanics expressions.[31] We have previously used this approach to calculate the heat of formation of NH_2OH,[32] as well as that of HNO. For NH_2OH, we obtained a value of -7.6 ± 0.3 kcal/mol at 0 K and -10.1 ± 0.3 kcal/mol at 298 K. These values fall between the experimental values of -12.0 ± 2.4 kcal/mol[33] and -7.9 ± 1.5 kcal/mol[34] at 298 K. Saraf et al.[35] have used a variety of computational approaches with isodesmic reactions to obtain a value of $\Delta H_f^{298K} = -11.4 \pm 0.6$ kcal/mol. For ΔH_f(HNO), we obtained 26.6 ± 0.2 and 25.9 ± 0.2 kcal/mol at 0 and 298 K, respectively, in comparison to the best experimental values[36] of 26.3 ± 0.03 and 25.6 ± 0.03 kcal/mol at 0 and 298 K, respectively. We have used even higher levels to calculate the heats of formation of the radicals NH_2 and OH.[24,25]

In the current study, we present high-level calculations at the CCSD(T) level with up through the aug-cc-pV5Z correlation consistent basis sets on the heats of formation and energetics of NH_2O, NH_2O^-, HONH, NH_2OH^+, HNO^-, and NH_3OH^+. In addition, we have used the COSMO model to predict the solvation energies of these species. Lind and Merenyi[37] have recently submitted an experimental study of the thermodynamic properties of NH_2O in aqueous solution.

Computational Approach

For the current study, we used the augmented correlation consistent basis sets aug-cc-pV*n*Z for H, O, and N (n = D, T, Q, 5). Only the spherical components (5-*d*, 7-*f*, 9-*g*, and 11-*h*) of the Cartesian basis functions were used. All of the current work was performed with the Gaussian98, MOLPRO, and NWChem suites of programs.[38] All of the MOLPRO and NWChem calculations were performed on a massively parallel 1980 processor HP Linux cluster with Itanium-2 processors, and the Gaussian-98 calculations were performed on a 16-processor SGI computer system.

The geometries were optimized at the frozen core CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ correlation-consistent basis sets and, in some cases, with the aug-cc-pVQZ basis sets. The vibrational frequencies were calculated at the MP2/cc-pVTZ level. The CCSD(T)/aug-cc-pVTZ geometries were then used in single-point CCSD(T)/aug-cc-pVQZ and CCSD(T)/aug-cc-pV5Z calculations. The open-shell CCSD(T) calculations for the atoms were performed at the R/UCCSD(T) level. In this approach, a restricted open-shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled-cluster calculation.[39−41] The CCSD(T) total energies were extrapolated to the CBS limit, using a mixed exponential/Gaussian function of the form

$$E(n) = E_{CBS} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (1)$$

with n = 2 (DZ), 3 (TZ), and 4(QZ), as first proposed by Peterson et al.[42] This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment by a small measure, as compared to other extrapolation approaches up through $n = 4$. In addition, we also used the following expansion in $1/\ell_{max}$ (where ℓ_{max} equals the highest angular momentum present in the basis set)[43] to estimate the complete basis set limit, using the aug-cc-pVQZ and aug-cc-pV5Z results:

$$E(\ell_{max}) = E_{CBS} + \frac{B}{\ell_{max}^{\ 3}} \quad (2)$$

TABLE 1. Optimized CCSD(T) Bond Lengths and Bond Angles for Different Molecules

basis set	bond lengths (Å)			bond angles (deg)	
	r(NO)	r(NH)	r(OH)	∠HNO	additional ∠
			NH_2O (nonplanar)		
aVDZ	1.2899	1.0221		118.23	154.85[a]
aVTZ	1.2801	1.0133		118.69	158.67[a]
aVQZ	1.2757	1.0118		118.87	160.58[a]
			NH_2O (planar)		
aVDZ	1.2865	1.0198		119.71	
aVTZ	1.2780	1.0117		119.77	
aVQZ	1.2739	1.0105		119.74	
			NH_2O^-		
aVDZ	1.4644	1.0408		105.67	106.79[a]
aVTZ	1.4527	1.0306		105.84	107.54[a]
			HNOH		
aVDZ	1.3844	1.0369	0.9705	100.22	103.39[b]
aVTZ	1.3767	1.0268	0.9657	100.58	103.47[b]
			NH_2OH^+		
aVDZ	1.3099	1.0262 1.0275	0.9847	113.79 121.52	109.74[b]
aVTZ	1.3006	1.0188 1.0195	0.9806	114.02 121.47	109.91[b]
			HNO^-		
aVDZ	1.3493	1.0628		105.55	
aVTZ	1.3398	1.0506		105.62	
			HON ($^3A''$)		
aVDZ	1.3492		0.9762		106.98[b]
aVTZ	1.3356		0.9716		107.22[b]
			NH_3OH^+		
aVDZ	1.4175	1.0323 1.0338(×2)	0.9781	104.48 111.55 (×2)	106.49[b]
aVTZ	1.4083	1.0261 1.0272(×2)	0.9735	104.73 111.60(×2)	106.57[b]

[a] Dihedral ∠HNOH. [b] ∠HON.

TABLE 2. Calculated MP2/cc-pVTZ Vibrational Frequencies for Different Molecules

symmetry	calculated vibrational frequency (cm^{-1})
NH_2O (planar)	
b_1	193.1
b_2	1276.9
a_1	1518.2
a_1	1689.3
a_1	3495.1
b_2	3646.4
NH_2O^-	
a′	858.5
a′	1168.2
a′	1194.9
a′	1589.5
a′	3179.3
a″	3254.4
NH_2OH^+	
a″	349.4
a″	736.0
a′	1201.2
a′	1458.0
a′	1530.1
a′	1688.9
a′	3491.2
a′	3625.9
a′	3666.8
HNOH	
a″	770.5
a′	1146.1
a′	1283.3
a′	1588.8
a′	3477.0
a′	3825.1
HNO^-	
a′	1182.0
a′	1447.6
a′	2924.7
HON($^3A''$)	
a′	1152.6
a′	1259.4
a′	3743.7
NH_3OH^+	
a″	309.1
a′	1061.1
a′	1163.1
a″	1197.4
a′	1500.6
a′	1574.8
a′	1668.1
a″	1670.1
a′	3382.0
a″	3482.7
a′	3494.0
a′	3743.5

Equation 2, or similar expansions in $1/\ell_{max}$, work well if aug-cc-pV5Z basis set (or higher) energies are available. Although eq 2 was originally proposed for describing only the correlation component of the total energy, we have used it to fit the total CCSD(T) energy, because the Hartree−Fock component of the CCSD(T) energy is very nearly converged for such large basis sets.

Core-valence corrections (ΔE_{CV}) were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[44] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI−SD (configuration interaction singles and doubles) level of theory, using the aug-cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[45] Most electronic structure computer codes do not correctly describe the lowest-energy spin multiplet of an atomic state. Instead, the energy is a weighted average of the available multiplets. For N in the ^4S state, no such correction is needed, but a correction of 0.22 kcal/mol is needed for O (taken from the excitation energies of Moore).[46]

The frequencies were calculated at the MP2/cc-pVTZ level. These frequencies were used to calculate the ZPEs. The ZPEs were scaled by 0.982, obtained as the ratio of the best estimate for the ZPE of HNO (8.56 kcal/mol, from the calculated quartic force field[47]) with the MP2 frequencies (1487, 1586, and 3029 cm^{-1}). We estimate that this introduces an error of ±0.5 kcal/mol.

By combining our computed $\sum D_0$ values with the known heats of formation at 0 K for the elements[48] ($\Delta H_f^0(N) = 112.53 \pm 0.02$ kcal/mol, $\Delta H_f^0(O) = 58.98$ kcal/mol, and $\Delta H_f^0(H) = 51.63$ kcal/mol), we can derive ΔH_f^0 values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[31]

Results and Discussion

The molecular geometries are given in Table 1. Only the geometry for NH_2O is known. Mikami et al.[18] assumed that the N−H bond is 1.01 Å and that the molecule has C_{2v} symmetry. This yields $r(NO) = 1.280 \pm 0.004$ Å and $\angle HNH° = 122.7 \pm 2.2°$, which are in good agreement with our values of $r(NO) = 1.2739$ Å and $\angle HNH = 120.5°$ that are obtained

TABLE 3. Components of the Calculated Atomization Energies[a]

							calculated atomization energy (kcal/mol)	
molecule	CBS, eq 1[b]	CBS, eq 2[c]	ΔE_{ZPE}[d]	ΔE_{CV}[e]	ΔE_{SR}[f]	ΔE_{SO}[g]	ΣD_0(0 K), eq 1[h]	ΣD_0(0 K), eq 2[i]
NH_2O (nonplanar)	274.10	273.91	−16.58	0.77	−0.50	−0.22	257.57	257.38
NH_2O (planar)	274.07	273.86	−16.58	0.78	−0.50	−0.22	257.55	257.34
NH_2O^-	278.95	279.05	−15.77	0.54	−0.48	−0.22	263.02	263.12
HNOH	267.13	267.01	−16.96	0.50	−0.43	−0.22	250.02	249.90
H_2NOH^+	145.90	145.57	−24.90	0.79	−0.53	−0.22	121.04	120.71
H_3NOH^+	248.03	247.78	−34.01	0.79	−0.53	−0.22	214.06	213.81
HNO^-	211.56	211.64	−7.79	0.47	−0.44	−0.22	203.58	203.66
HNO	205.07	204.98	−8.56	0.40	−0.33	−0.22	196.36	196.27
HON	179.40	179.26	−8.64	0.38	−0.35	−0.22	170.57	170.43

[a] Open-shell species, including the atomic asymptotes, were calculated with the R/UCCSD(T) method. [b] Extrapolated using eq 1 with aD, aT, aQ. [c] Extrapolated using eq 2 with aQ, a5. [d] Zero-point energies (ZPEs) were obtained by scaling the MP2/cc-pVTZ values by 0.982, except for HNO, which is taken from ref 47. See text for details. [e] Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the CCSD(T) level. [f] The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ MVD calculation. [g] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables in ref 46. [h] ΣD_0(0 K) computed with the extrapolated value from eq 1. [i] ΣD_0(0 K) computed with the extrapolated value from eq 2.

TABLE 4. Calculated Heats of Formation Based on the Average of the ΣD_0(0 K) Values from eqs 1 and 2[a]

molecule	ΔH_f(0 K) (kcal/mol)	ΔH_f(298 K) (kcal/mol)
NH_2O	17.3 ± 0.8	16.0 ± 0.8
NH_2O-	11.6 ± 0.8	10.0 ± 0.8
HNOH	24.8 ± 0.8	23.1 ± 0.8
NH_2OH^+	205.5 ± 0.8	203.1 ± 0.8
NH_2OH[b]	−7.6 ± 0.3	−10.1 ± 0.3
NH_3OH^+	164.1 ± 0.8	160.7 ± 0.8
HNO^-	19.5 ± 0.5	18.8 ± 0.5
HNO	26.8 ± 0.5	26.1 ± 0.5
HON	52.6 ± 0.5	51.9 ± 0.5
NO[c]	22.2 ± 0.5	22.3 ± 0.5

[a] Experimental heats of formation of H^+ are 365.2 and 365.7 kcal/mol at 0 and 298 K, respectively. Experimental heat of formation of atomic hydrogen (H) at 298 K is 52.10 kcal/mol. [b] Ref 32. [c] Ref 50.

at the CCSD(T)/aug-cc-pVQZ level, which are both smaller than the experimental values. The molecule is essentially planar. The electronic energy difference is 0.02 kcal/mol using eq 1 and 0.03 kcal/mol using eq 2. If the molecule is nonplanar, the inversion frequency will be above the barrier to planarity, so the molecule will have an average planar structure.

The calculated MP2 vibrational frequencies are given in Table 2. The total energies are given as Supporting Information. The various energy components used in calculating the total dissociation energy to atoms, as shown in eq 3,

$$\Sigma D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} \quad (3)$$

are given in Table 3. We estimate that there is an error of ±0.3 kcal/mol in the electronic energy components (±0.2 kcal/mol from the extrapolation based on the spread in the two extrapolated values and ±0.1 from the remaining terms) and, together with the maximum ZPE error, we obtain a maximum error of ±0.8 kcal/mol.

The calculated heats of formation are given in Table 4. Our calculated value for ΔH_f(HNO) is within 0.2 kcal/mol of our value calculated with basis sets up through the aug-cc-pV6Z basis set. Our calculated heat of formation for NH_2O, 17.3 ± 0.8 kcal/mol, is in good agreement with the value of 17.9 kcal/mol of Soto et al.[16] Stipa[49] reported that the calculated heat of formation for NH_2O at 298 K was 13.7 kcal/mol for the CBS-QB3 method. At 298 K, we calculate the heat of formation for NH_2O to be 16.0 kcal/mol, and the lower level CBS-Q3 result differs from our higher level calculation by more than 2 kcal/mol. Our calculated energy difference between NH_2O and HNOH is 7.5 kcal/mol at 0 K, compared to the value of 5.8 kcal/mol obtained by Soto et al.[16] This difference is somewhat larger than would have been expected based on the levels of calculation used by Soto et al.[16]

The various total energies and heats of formation can be used to calculate a range of interesting energetic quantities for these species. The electron affinity of NH_2O is calculated to be 5.45 kcal/mol (0.24 eV) using eq 1 for the CBS extrapolation and 5.74 kcal/mol (0.25 eV) using eq 2 for the CBS extrapolation. The electron affinity of HNO is calculated to be 7.22 kcal/mol (0.31 eV) using eq 1 and 7.39 kcal/mol (0.32 eV) using eq 2. These electron affinities are not large but are substantially larger than that for NO, which is calculated to be 0.62 kcal/mol.[50] The ionization potential of NH_2OH is calculated to be 213.1 kcal/mol (9.24 eV).

The gas-phase acidities, defined as ΔH for the reaction AH $\rightarrow A^- + H^+$, are given in Table 5. The gas-phase acidity of NH_2O ($NH_2O \rightarrow HNO^- + H^+$) is 367.4 kcal/mol at 0 K and 368.5 kcal/mol at 298 K. Thus, it is a stronger acid in the gas phase, compared to H_2O, with an acidity of 390.3 kcal/mol at 298 K.[51] The proton affinity of NH_2O is 177.1 kcal/mol at 0 K and 178.7 kcal/mol at 298 K. Thus, NH_2O is a stronger gas-phase base than H_2O, which has a proton affinity of 165 kcal/mol but a substantially weaker base than NH_3 which has a proton affinity[24] of 204 kcal/mol. The acidity of NH_2OH (ΔH for the reaction $NH_2OH \rightarrow NH_2O^- + H^+$) is 384.4 kcal/mol at 0 K and 385.8 kcal/mol at 298 K and is substantially higher than that of NH_2O, showing that it is a very weak acid. In fact, the gas-phase acidity for NH_2OH is comparable to that of H_2O, being only 4.6 kcal/mol stronger. The proton affinity of NH_2OH in the gas phase is 194.9 kcal/mol at 298 K, which is somewhat lower than the value for NH_3, as expected when substituting the electronegative OH group for H.

Various bond dissociation energies are given in Table 6. The bond energy of the O−H bond in NH_2OH is 76.5 kcal/mol at 0 K. Breaking the N−H bond requires 84.0 kcal/mol at 0 K. Lind and Merenyi[37] estimate the gas-phase OH bond energy from the solution energetics to be 75−77 kcal/mol. For the N−H bond energy, they estimate a range of 81−82 kcal/mol. The present calculations are in excellent agreement with these new experimental estimates. Because of the instability of HNOH, as compared to NH_2O, the N−H bond is stronger than the O−H bond, reversing the usual trend that O−H bonds are usually stronger than N−H bonds. We do note that the OH bond in NH_2OH is much weaker than the OH bond in H_2O and that the N−H bond in NH_2OH is weaker than the N−H bond in NH_3.

TABLE 5. Enthalpies and Free Energies of Proton Loss Reactions

		free energy of proton loss reaction (kcal/mol)				
reaction	enthalpy, ΔH(gas, 298 K) (kcal/mol)	ΔG(gas, 298 K)	ΔG(solv, 298 K) PCM	ΔG(aq, 298 K) PCM	ΔG(solv, 298 K) COSMO	ΔG(aq, 298 K) COSMO
$NH_2OH \rightarrow H^+ + NH_2O^-$	385.8	378.5	−339.4	39.1	−343.7	34.8
$NH_2O \rightarrow H^+ + HNO^-$	368.5	361.6	−327.7	33.9	−329.3	32.3
$NH_2OH^+ \rightarrow H^+ + NH_2O$	178.6	170.8	−185.9	−15.1	−191.1	−20.3
$NH_3OH^+ \rightarrow H^+ + NH_2OH$	194.9	187.4	−186.1	1.3	−183.1	4.3
$H_2O \rightarrow H^+ + HO^-$	390.2[a]	383.7[a]	−340.6	43.1	−345.2	38.5

[a] Refs 25, 48, and 51.

TABLE 6. Bond Energies at 0 K[a]

	bond energy (kcal/mol)		
molecule	O−H	N−H	N−O
NH_2OH	76.5	84.0	61.7
NH_2O		61.1	87.0
HNOH	79.4	53.6	70.0
HNO		47.0	118.1
HON	21.2		68.8

[a] Calculated heat of formation at 0 K for NH_2 is 45.27 kcal/mol and for NH is 85.92 kcal/mol from ref 24. Calculated heat of formation at 0 K for OH is 8.85 kcal/mol (from ref 25).

The bond energy for breaking the N−H bond in NH_2O is 61.1 kcal/mol. The bond energy for breaking the O−H bond in HNOH is only 53.6 kcal/mol, and the N−H bond energy is higher at 79.4 kcal/mol, because of the instability of HON. The H−N bond energy in HNO is 47.0 kcal/mol, and the O−H bond energy in HON is much lower, at 21.2 kcal/mol.

The N−O bond energies in the various species can be calculated from the data in this paper and the heats of formation of various fragments that we have previously calculated at high levels.[24,25,50] The N−O bond energy in NH_2O (producing the O atom) is 87.0 kcal/mol and is higher than the N−O bond energies in NH_2OH and HNOH, which yield the OH radical as a product. The NO bond energy in NH_2O is substantially lower than that in HNO, which is consistent with the higher N−O bond order in the latter. The N−O bond energy in HON is comparable to that in HNOH, and, in both cases, an OH radical is formed.

We are also interested in the behavior of these species in aqueous solutions, especially for comparison to the work of Lind and Merenyi.[37] To estimate the effects of solvation, we have calculated the free energies of solvation using the PCM[52] and COSMO[53] approaches. We have chosen these solvation approaches for their simplicity and because they have been used in previous studies of the solvation of similar NO_xH_y species.[54] The solvation calculations were conducted at the density functional theory level with the B3LYP functional and the 6-311+G(d) basis set. This approach is simpler than the combined supermolecule-continuum approach that we have used previously to calculate the free energy of solvation of the proton in aqueous solution.[55] At 298 K, the value of $\Delta G_{\mathrm{solv}}(H^+)$ is −262.4 kcal/mol, and we can use this value together with the gas-phase acidities and the calculated free energies of solvation of the neutral acid and the anion to estimate the pK_a values in aqueous solution at 298 K. These methods seem to work well with larger anions but not as well with smaller anions.[50,56]

The experimental value for ΔG for the reaction $H_2O \rightarrow OH^- + H^+$ in the gas phase is −383.6 kcal/mol at 298 K.[51] Using this value, together with the COSMO values for the free energy of solvation of H_2O and OH^- (Table 7), we obtain pK_a = 28.2 for 1 M H_2O (Table 8) and a value of pK_a = 31.6 at the PCM level. The calculated values for pK_a(H_2O) are clearly different from the well-established value of pK_a = 15.7, corrected for the H_2O concentration of 55.4 M. Thus, our simple solvation approach is making a substantial error of 12 to 13 pK_a units for H_2O at the COSMO level and a larger error at the PCM level. This error is due to the lack of explicit waters of solvation around the OH^-. If these are included, excellent agreement with the experiment is observed, but a substantial number of water molecules are required.[57]

TABLE 7. Calculated Entropy (S^{298K}) and PCM and COSMO Solvation Energy Values[a]

		solvation energy (kcal/mol)	
molecule	S^{298K} (cal mol^{-1} K^{-1})	PCM	COSMO
NH_2O	57.37	−12.66	−11.85
NH_2O^-	54.60	−88.09	−90.19
HNOH	55.71	−11.66	−7.78
NH_2OH^+	57.40	−89.12	−83.92
NH_2OH	56.05	−11.08	−8.93
NH_3OH^+	56.96	−87.38	−88.19
HNO^-	54.55	−77.92	−78.73
HNO	52.77	−7.68	−5.78
NOH	55.14	−11.65	−7.79
OH^-	41.22[b]	−89.11	−93.37
H_2O	45.13[b]	−10.94	−10.54

[a] Free energy of solvation of the proton is −262.4 kcal/mol (from ref 55). $S^{298K}(H^+)$ = 26.04 cal mol^{-1} K^{-1} (from refs 48 and 51). [b] From refs 48 and 51.

TABLE 8. Calculated and Experimental pK_a Values

	pK_a		adjusted[a] pK_a		
reaction	PCM	COSMO	PCM	COSMO	exptl pK_a
$NH_2OH \rightarrow H^+ + NH_2O^-$	28.7	25.5	12.8	13.0	13.74[a]
$NH_2O \rightarrow H^+ + HNO^-$	24.9	23.7	9.0	11.2	12.6 ± 0.3[b]
$H_2O \rightarrow H^+ + HO^-$	31.6	28.2			15.7[c]
$NH_2OH^+ \rightarrow H^+ + NH_2O$	−11.1	−14.8	−3.9	−5.4	−7 ± 2[b]
$NH_3OH^+ \rightarrow H^+ + NH_2OH$	−1.0	−3.2			6.17[d]

[a] Adjusted to the experimental value for H_2O for the acidities and to the experimental value for NH_3OH^+ for the basicities. See text and ref 59. [b] Data taken from ref 37. [c] Corrected for H_2O concentration [d] Data taken from ref 10.

The calculated entropies at 298 K and free energies of solvation are given in Table 7. The calculated reaction free energies are given in Table 6, and the pK_a values are given in Table 8. First, we note that the effect of solvation is to make the energy difference between NH_2O and HNOH larger in solution than in the gas phase. Thus, at equilibrium in solution, only NH_2O would be predicted to be observed. This is consistent with EPR results from the study of one-electron oxidation of hydroxylamine by Ce^{4+}, which show that NH_2O is the sole species and show no evidence of the HNOH isomer.[58]

The acidity of NH_2OH without any corrections gives pK_a = 25.5 at the COSMO level. This is clearly too high, in comparison to the experimental result of pK_a = 13.74.[59] The calculated pK_a is predicted to be 2.7 pK units smaller than that for H_2O at the COSMO level and 2.9 pK units at the PCM level, in reasonable agreement with the experimental difference of ~2 pK_a units.

This suggests that the solvation energy difference between NH_2OH and NH_2O^- is very similar to that between H_2O and OH^-. The approach of directly comparing the acidities to that of H_2O follows on the work of Pliego and Riveros[60] and Takano and Houk.[61] Using this approach, we predict $pK_a(NH_2OH)$ to be 13.0 at the COSMO level and 12.8 at the PCM level. The pK_a for NH_2O is predicted to be 1.8 pK_a units lower than that of NH_2OH at the COSMO level, which is consistent with the experimental value, which places it 1.1 ± 0.3 pK units lower. At the PCM level, the difference is somewhat larger (3.8 pK units). These results again suggest that the solvation energy differences between the neutrals and the anions are comparable for NH_2O/HNO^- and H_2O/OH^-.

Based on the calculated values, we would predict that NH_2OH^+ will not be formed in aqueous solution, because it has a low basicity, based on the predicted pK_a of -14.9 at the COSMO level and -11.1 at the PCM level, and will readily give up its proton. The raw PCM value is closer to the estimated experimental value of $pK_a = -7 \pm 2$.[37] We can use the same approach given above for the acidity of the neutral to compare the pK_a values of the cations. The experimental pK_a value of NH_3OH^+, which has been determined by Hung et al.,[10] is 6.17. The calculated difference in the pK_a values of NH_3OH^+ and NH_2OH^+ is 11.6 at the COSMO level and 10.1 at the PCM level. Using the value of 6.2 for $pK_a(NH_3OH^+)$, we obtain $pK_a(NH_2OH^+) = -5.4$ at the COSMO level and -3.9 at the PCM level. The COSMO value is within the experimental error bars and the PCM value is not negative enough. The computational results confirm the estimated experimental values. Thus, the COSMO model works better than the PCM model for predicting the pK_a value of the cations just as found for the neutrals. The computational and experimental results are consistent in showing that NH_2OH^+ will not be formed in aqueous solution at pH values relevant to biological processes and can only be formed under very acidic conditions in any case.

Conclusion

The NH_2O radical is an important intermediate involved not only in atmospheric reactions in the oxidation of ammonia (NH_3), but also as a key species involved in redox reactions involving hydroxylamine (NH_2OH) and the biologically important intermediate nitroxyl (HNO). Surprisingly, accurate thermodynamic data, which can assist in understanding the important chemical links between these species in the gas phase and the solution phase, have not been available. Accurate gas-phase thermodynamic data have been presented above for the NH_2OH, NH_2O, HNOH, HNO, and HON species. The electron affinities of NH_2O and HNO are small but are larger than that for NO. The present work shows that the NH_2O radical in solution is unprotonated, with a pK_a value much less than 0. The absolute predicted pK_a values are in error, with respect to experiment, without accounting for additional corrections. However, this error can be substantially reduced by predicting pK_a values with respect to that of H_2O. It is clear that the solvation of NH_2O^- must be similar to that of OH^- and is substantially higher than what is given by a solvation model without explicit solvent molecules. Yet, HNO^- is treated modestly well by simple solvation models.[50] These results show that our understanding of solvation effects for predicting pK_a values still needs to be improved.

NH_3 is important for the neutralization of acidic aerosols and water droplets in the atmosphere. However, there are many uncertainties in the aqueous chemistry by which this occurs. An important oxidation byproduct of NH_3 is the NH_2O radical. No experimental data are yet available on the important reactions of NH_2O on atmospheric aerosol surfaces. To explain NO_x budgets, modeling studies do indicate the importance of heterogeneous loss processes involving NH_3 and NH_2O. The present work has estimated important gas-phase and aqueous chemical energetics and pK_a values that can assist new experimental studies in evaluating important underlying processing chemistry in aerosols. For example, an important issue for atmospheric model studies is understanding the importance of NH_2O and its isomer HNOH in chemical schemes both in the gas phase and in aerosol form. The present work provides new insight into the dichotomy of NH_2O and HNOH in the chemistry in aerosol form and water droplets. If HNOH is important, it is only as a kinetic product, because, under equilibrium conditions in the atmosphere, as either a gas or in aerosol or droplet form, it will not be present.

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Supporting Information Available: Total CCSD(T) energies (E_h) as a function of basis set and extrapolated to the complete basis set limit (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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