Matrix Isolation and ab Initio Study of 1:1 Hydrogen-Bonded Complexes of H_2O_2 with NH_3 and $N(CH_3)_3$

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Matrix isolation infrared spectroscopy has been combined with MP2/6-31+G(d,p) calculations to characterize the 1:1 hydrogen-bonded complexes between H_2O_2 and the bases NH_3 and $N(CH_3)_3$. Most obvious from the spectra of these complexes and their deuterated analogues is the shift to lower frequency of the hydrogen-bonded O−H or O−D stretching bands relative to the isolated monomers. The experimental shifts are in good agreement with the computed shifts. Perturbation of the O−O−H bending mode was also observed, along with shifts of certain vibrational modes of the base subunits in the complexes. Surprisingly, the experimental intensities of the product bands are low when compared to other hydrogen-bonded systems and to the computed intensities.

Introduction

Hydrogen peroxide is a molecule that is of interest in a large and diverse number of fields, including atmospheric chemistry and biochemistry.[1−3] Gas-phase, solvent-free studies of H_2O_2 are technically difficult and solution studies are complicated by the role of the solvent, so that the role of hydrogen bonding in the chemistry of hydrogen peroxide is not well understood. On the other hand, theoretical studies[4,5] have characterized transition states and intermediates in the reaction chemistry of H_2O_2, but have not focused on hydrogen bond formation.

The matrix isolation technique[6,7] was developed for the isolation, stabilization, and spectroscopic characterization of reactive intermediates, including hydrogen-bonded complexes. Following the development[8] of the use of the hydrogen peroxide−urea complex (UHP) as a safe source of solvent-free gas-phase H_2O_2, a study was conducted in this laboratory to characterize the hydrogen bonding interaction of H_2O_2 with dimethyl ether.[9] Ab initio calculations were also carried out for this system to provide energetic and structural information for H_2O_2:$O(CH_3)_2$. Nitrogen bases,[10] including NH_3 and $N(CH_3)_3$, are stronger Lewis bases than $O(CH_3)_2$, and their interactions with proton donor molecules have been well studied.[11−17] Not only have traditional hydrogen-bonded complexes been observed, but complexes with proton-shared and ion-pair hydrogen bonds have been seen as well. In our continuing study of the hydrogen bonding capability of H_2O_2, a study has been undertaken to investigate hydrogen bond formation between H_2O_2 and the nitrogen bases NH_3 and $N(CH_3)_3$. Ab initio calculations have also been carried out to determine the structures and binding energies and enthalpies of these complexes, and to assist in the interpretation of the experimental spectra.

Experimental Section

All of the experiments in this study were carried out on conventional matrix isolation equipment,[18] with modification for the generation and deposition of H_2O_2 as has been described.[9] The temperature range for the vaporization of H_2O_2 in these experiments was 9−18 °C. NH_3 (Matheson), ND_3 (Isotec, 99% D), $N(CH_3)_3$ (Aldrich), and $N(CD_3)_3$ (MSD Isotopes, 99% D) were all introduced into the vacuum system from lecture bottles, and purified by repeated freeze−pump−thaw cycles at 77 K. Argon and nitrogen were used without further purification as the matrix gases in these experiments.

All of the experiments were conducted in the twin jet mode, where samples of H_2O_2 and the base were each diluted in the appropriate matrix gas and deposited from separate deposition lines onto the 14 K cold window. In the early experiments, a traditional slow deposition rate of approximately 2 mmol/h from each manifold for 22−24 h was used. Later experiments were conducted using a fast deposition of approximately 15 mmol/h from each manifold for 3 h. Spectra were then recorded on a Mattson Cygnus FTIR at 1 cm^{-1} resolution. Many of the matrices were subsequently annealed to between 30 and 36 K for argon matrices, and 25 and 27 K for N_2 matrices. After re-cooling, additional spectra were recorded.

Method of Calculation

Ab initio calculations at second-order Moller−Plesset perturbation theory [MBPT(2) = MP2][19−22] have been carried out with the 6-31+G(d,p) basis set[23−26] to determine the optimized structures of the complexes HOOH:NH_3 and HOOH:$N(CH_3)_3$, and of the corresponding monomers HOOH, NH_3, and $N(CH_3)_3$. The MP2/6-31+G(d,p) level of theory provides structures which are in reasonable agreement with experimental data, and is the minimum level of theory required to obtain frequency shifts of the hydrogen-bonded X−H stretching band in an X−H−Y

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hydrogen bond, provided that anharmonicity effects are not unusually large.[27−29] For improved energetics, single-point calculations were carried out on monomers and complexes at MP2 with the Dunning correlation-consistent polarized valence triple-split basis set[30−32] with diffuse functions only on nonhydrogen atoms (aug′-cc-pVTZ). Harmonic vibrational frequencies were computed to establish that all structures are equilibrium structures on their respective potential energy surfaces, to obtain zero-point vibrational energies, and to simulate the vibrational spectra of the complexes. The vibrational spectra of the deuterated analogues of these complexes were also obtained. For all calculations, 1s core electrons were frozen in the Hartree−Fock molecular orbitals. All calculations were carried out using the Gaussian 98 suite of programs[33] on the Cray T94 computer at the Ohio Supercomputer Center.

Results

Before codeposition experiments were run, blank spectra were recorded of each of the reagents alone in each of the matrices. The spectra were in very good agreement with literature spectra,[8,14,34] and with spectra recorded previously in this laboratory.[9] All H_2O_2 experiments contained observable amounts of $(H_2O_2)_2$, particularly at higher vaporization temperatures. However, H_2O_2 monomer was still the predominant species in all of these experiments.

$H_2O_2 + NH_3$. Initial experiments with this pair of reagents were carried out in argon matrices using slow deposition. These experiments were relatively unsuccessful, with a high degree of scattering in the high-energy region (>3000 cm^{-1}), and no detectable product. As a result, experiments employing fast deposition were undertaken. This approach leads to higher quality, more uniform matrices due to the longer freezing time required for the higher mass (and heat) load on the cold window. However, the blank spectra demonstrate that a good degree of monomer isolation is still achieved.

In an initial fast deposition experiment, argon swept over UHP @ 18 °C was co-deposited with a sample of $Ar/NH_3 = 1000/1$. Several distinct product bands were noted, including two weak, fairly broad bands at 3232 and 2913 cm^{-1}. The other product band was a sharp band with medium intensity at 1051 cm^{-1}. This spectrum is shown in Figure 1. Upon annealing this matrix to 36 K all the product bands grew to some extent.

A total of seven additional experiments with argon as the matrix gas were then conducted in which the temperature of the UHP (and thus the concentration of H_2O_2) was varied from 9 °C to 18 °C and the NH_3 concentration varied from $Ar/NH_3 = 1000/1$ to 500/1. In all of these experiments, the bands at 3232, 2913, and 1051 cm^{-1} were present with intensities that varied directly with the concentrations of the reactants. No new product bands were formed in any of these experiments. Annealing was performed on five of the seven matrices with the product bands growing only slightly in all the annealed matrices.

Because of the rotational substructure in the spectrum of NH_3 in argon matrices,[14] and the lack of this substructure in N_2 matrices, experiments were also conducted using nitrogen as the matrix material. In an initial experiment nitrogen swept over UHP at 9 °C was co-deposited with a sample of $N_2/NH_3 = 500/1$. Several distinct product bands were noted, including three weak, fairly broad bands at 3188, 3128, and 2937 cm^{-1}. Additional product bands included a weak band at 1066 cm^{-1} and three very weak bands at 1307, 1305, and 1075 cm^{-1}. Upon annealing the matrix, the product bands grew a small amount except for the band at 2937 cm^{-1} that remained constant, and the band at 1075 cm^{-1} that disappeared. One new, very weak band appeared at 1072 cm^{-1} in the annealed matrix.

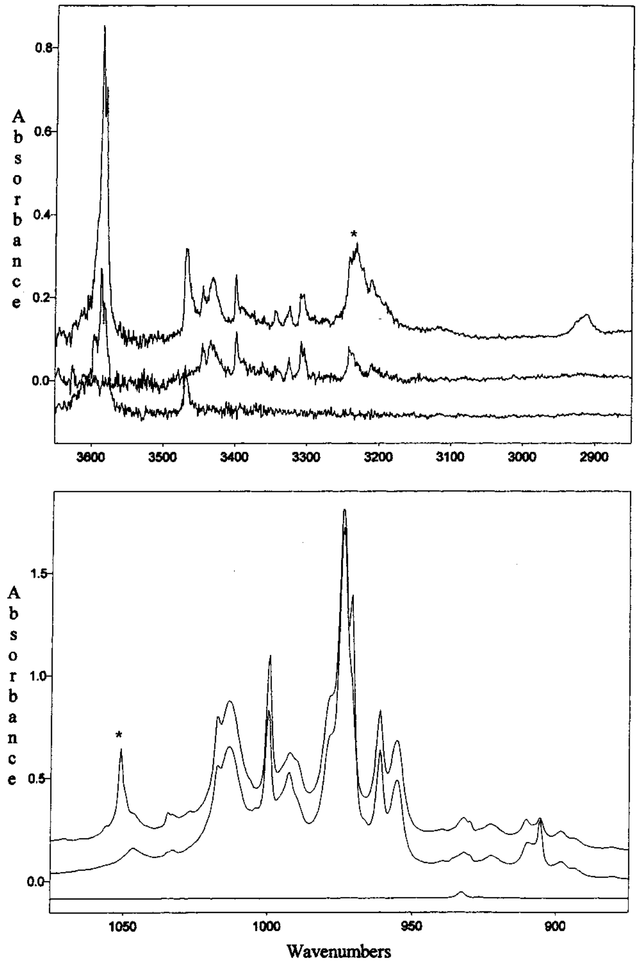

Figure 1. Infrared spectrum of a matrix prepared by passing argon over the solid H_2O_2:urea complex, and co-depositing with a sample of $Ar/NH_3 = 1000/1$ (top trace) compared to a blank spectrum of $Ar/NH_3 = 1000$ (middle trace) and a matrix of $Ar + H_2O_2$ (bottom trace). Bands marked with an * are due to the 1:1 hydrogen-bonded complex.

Four additional experiments with nitrogen as the matrix gas were then conducted in which the temperature of the UHP was varied from 12 °C to 15 °C and the N_2/NH_3 concentration varied from 1000/1 to 500/1. In all of these experiments, the bands at 3188, 3128, 2937, 1307, 1305, 1075, and 1066 cm^{-1} were present with intensities that varied directly with the concentrations of the reactants. No new product bands were formed in any of these experiments. Annealing was again performed on all four matrices with the same results as in the initial experiment.

$D_2O_2 + NH_3$. In an initial experiment argon swept over d_2-UHP at 18 °C was co-deposited with a sample of $Ar/NH_3 = 500/1$. Several distinct product bands were noted including a fairly broad band at 2391 and a strong band at 1051 cm^{-1}. Both product bands grew slightly upon annealing. In an initial N_2 matrix experiment, nitrogen swept over d_2-UHP at 18 °C was co-deposited with a sample of $N_2/NH_3 = 500/1$. Three weak product bands were seen at 2332, 1066, and 1075 cm^{-1}. Upon annealing this matrix the product bands at 2332 and 1066 cm^{-1} grew somewhat, the band at 1075 cm^{-1} disappeared, and a very weak band at 1072 cm^{-1} appeared. Three additional experiments were then run with nitrogen as the matrix gas. The N_2/NH_3 concentration was held constant at 500/1 and the d_2-UHP temperature was 12 °C in one experiment and 15 °C in the other

TABLE 1: Band Positions (cm^{-1}) and Assignments for the 1:1 Complex of H_2O_2 with NH_3 in a Nitrogen Matrix

H_2O_2:NH_3	H_2O_2:ND_3	D_2O_2:NH_3	D_2O_2:ND_3	assignment
1066, 1075	993	1066, 1075	993	ν_2, NH_3 def. (NH_2D)^a sym
1305, 1307	1305, 1307			O−O−H bend
3128, 3188	3121, 3185	2332	2332	ν_s, O−H (O−D) stretch

[a] In matrices containing ND_3, NHD_2, and NH_2D were also present due to exchange. ND_3 was the dominant species. The regions where ν_2 for the complexes HOOH:ND_3 and HOOH:NHD_2 is expected were too congested to observe a product band. Since NH_2D was present in lesser amounts, the shifted ν_2 band for the complex HOOH:NH_2D was observable.

two. In addition to the bands previously seen at 2332, 1066, and 1075 cm^{-1}, a very weak band was observed at 598 cm^{-1}.

H_2O_2 + ND_3. In the initial experiment nitrogen swept over UHP at 15 °C was co-deposited with a sample of N_2/ND_3 = 500/1. Several distinct product bands were observed, including three weak, fairly broad bands at 3185, 3121, and 2936 cm^{-1}. The other product bands were three very weak bands at 1307, 1305, and 993 cm^{-1}. Upon annealing the matrix, the product bands grew slightly except for the band at 2936 cm^{-1} that remained constant.

Two additional experiments with nitrogen as the matrix gas were then conducted in which the temperature of the UHP was 9 °C and the N_2/ND_3 concentration varied from 500/1 to 1000/1. In both of these experiments, the bands at 3185, 3121, 2936, 1307, 1305, and 993 cm^{-1} were present with intensities that varied directly with the concentrations of the reactants. Annealing of these matrices gave the same results as the initial experiment.

D_2O_2 + ND_3. In one experiment, nitrogen swept over d$_2$-UHP at 15 °C was co-deposited with a sample of N_2/ND_3 = 500/1. Several distinct product bands were noted including weak, fairly broad bands at 2332 and 2936 cm^{-1}. The other product band was a very weak band at 993 cm^{-1}. Upon annealing the matrix, the product bands grew slightly except for the band at 2936 cm^{-1} that remained constant. Table 1 summarizes the experimental band positions for the reactions of H_2O_2 and D_2O_2 with NH_3 and ND_3.

H_2O_2 + $N(CH_3)_3$. Just as in the experiments with NH_3, initial experiments were conducted using slow deposition of argon matrices. These did not produce any new features in the resulting spectrum. Guided by the NH_3 experiments, all of the remaining experiments involving $N(CH_3)_3$ were carried out in N_2 matrices using fast deposition. In an initial experiment, nitrogen swept over UHP at 15 °C was co-deposited with a sample of $N_2/N(CH_3)_3$ = 250/1. No product bands were seen in the resulting spectrum. Given the relative basicities[10] of NH_3 and $N(CH_3)_3$, it appeared likely that the most intense product bands would occur in the region overlapping the numerous C−H stretching modes of $N(CH_3)_3$. To eliminate this difficulty, H_2O_2 was reacted only with $N(CD_3)_3$, and D_2O_2 only with $N(CH_3)_3$.

H_2O_2 + $N(CD_3)_3$. In an initial experiment nitrogen swept over UHP at 15 °C was co-deposited with a sample of $N_2/N(CD_3)_3$ = 250/1. Several distinct product bands were noted, including three fairly broad bands at 2913, 2847, and 2771 cm^{-1}. The other product bands were a band at 1032 cm^{-1} and two very weak bands at 1312 and 1028 cm^{-1}, as shown in Figure 2. Upon annealing the matrix, all of these product bands grew in roughly the same proportions except for the band at 2913 cm^{-1}, which did not grow significantly. The band at 2847 cm^{-1} separated into two partially resolved bands at 2853 and 2836 cm^{-1}. In addition, a broad feature centered at 3114 cm^{-1} which seemed to consist of several unresolved bands, appeared upon annealing.

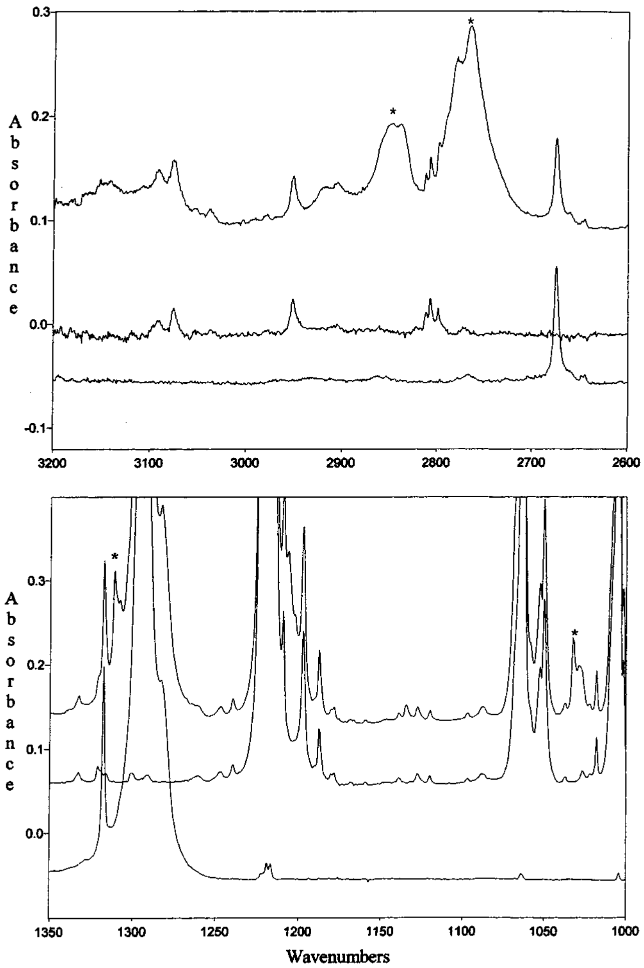

Figure 2. Infrared spectrum of a matrix prepared by passing N_2 over the solid H_2O_2:urea complex and co-depositing with a sample of $N_2/N(CH_3)_3$ = 250/1 (top trace) compared to a blank spectrum of $N_2/N(CD_3)_3$ = 250 (middle trace) and a matrix of N_2 + H_2O_2 (bottom trace). Bands marked with an * are due to the 1:1 hydrogen-bonded complex.

Nine additional experiments were then conducted in which the temperature of the UHP was varied from 9 °C to 15 °C and the $N_2/N(CD_3)_3$ concentration varied from 250/1 to 500/1. In all of these experiments, the same product bands were present with intensities that varied directly with the concentrations of the reactants. The same results were obtained upon annealing as in the initial experiment.

D_2O_2 + $N(CH_3)_3$. In an initial experiment nitrogen swept over d$_2$-UHP at 15 °C was co-deposited with a sample of $N_2/N(CH_3)_3$ = 250/1. Several distinct product bands were noted, including a very broad feature (consisting of several partially resolved bands) centered at 2283 cm^{-1}, and another broad feature centered at 2108 cm^{-1}. This second feature consisted of at least three bands with maxima located at 2129, 2115, and 2085 cm^{-1}. There were also one medium intensity band at 2032 cm^{-1} and two weaker bands at 811 and 808 cm^{-1}. Upon annealing the matrix, all of the product bands grew very slightly in roughly the same proportion, except for the band at 2032 cm^{-1} which decreased.

Four additional experiments were then conducted in which the temperature of the d$_2$-UHP was varied from 12 °C to 18 °C and the $N_2/N(CH_3)_3$ concentration varied from 250/1 to 500/1.

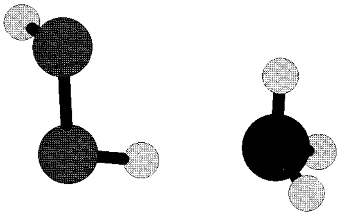

Figure 3. Structure of the HOOH:NH_3 complex, computed at the MP2/6-31+G(d,p) level of theory. Key structural parameters are given in the text.

TABLE 2: Band Positions (cm^{-1}) and Assignments for the 1:1 Complex of H_2O_2 with $N(CH_3)_3$ in a Nitrogen Matrix

H_2O_2:$N(CD_3)_3$	D_2O_2:$N(CH_3)_3$	assignments
1028, 1032	808, 811	see text
1312		O−O−H bend
2771, 2847	2108	ν_s, O−H (O−D) stretch

In all of these experiments, the same product bands were present with intensities that varied directly with the concentrations of the reactants. Upon annealing the same results were obtained as in the first experiment. Table 2 summarizes band positions arising from the co-deposition of H_2O_2 with $N(CD_3)_3$ and D_2O_2 with $N(CH_3)_3$.

Results of ab Initio Calculations

A search of the HOOH:NH_3 potential surface yielded only one equilibrium structure, which is stabilized by an O−H···N hydrogen bond. The intermolecular O−N distance in this complex is 2.810 Å, and the hydrogen bond is slightly nonlinear, with an angle of 8° between the hydrogen-bonded O−H bond and the intermolecular O−N line. The hydrogen-bonded O−H distance in this complex is 0.990 Å, a lengthening of 0.020 Å relative to the monomer, as shown in Figure 3. Similarly, there is only one equilibrium structure for HOOH:$N(CH_3)_3$. This complex has a linear O−H···N hydrogen bond, with a shorter intermolecular O−N distance of 2.727 Å and a hydrogen-bonded O−H distance of 1.004 Å.

The MP2/aug′-cc-pVTZ electronic binding energy (ΔE_e) of HOOH:NH_3 is −9.0 kcal/mol. When zero-point energy differences are applied, the binding enthalpies ($\Delta H°$) of this complex and its isotopomers [HOOH:ND_3 , DOOD:NH_3, and DOOD:ND_3] are −6.7, −7.1, −6.9, and −7.2 kcal/mol, respectively. The complex HOOH:$N(CH_3)_3$ is stabilized by a stronger hydrogen bond, with an MP2/aug′-cc-pVTZ electronic binding energy (ΔE_e) of −11.3 kcal/mol. The binding enthalpies ($\Delta H°$) of HOOH:$N(CH_3)_3$, HOOH:$N(CD_3)_3$, and DOOD:$N(CH_3)_3$ are −9.8, −9.9, and −9.8 kcal/mol, respectively. Anharmonic corrections have been investigated for the related ClH:NH_3 complex and were found[17] to be less than 0.2 kcal/mol. The corrections are expected to be less for the present complexes.

Discussion

TABLE 3: Experimental and Computed Band Shifts for ν_s of H_2O_2:NH_3 and H_2O_2:$N(CH_3)_3$

complex	computed shift	Ar matrix shift	N_2 matrix shift[a]
HOOH:NH_3	−400 cm^{-1}	−351	-424
DOOD:NH_3	−288	−253	−312
HOOH:ND_3	−400		−429
DOOD:ND_3	−289		−312
HOOH:$N(CD_3)_3$	−683		−773
DOOD:$N(CH_3)_3$	−490		−448

[a] Where multiplets were observed experimentally (see Tables 1 and 2), the average band position was used to determine the shift.

Product Identification. While the overall product yield arising from the co-deposition of H_2O_2 with both NH_3 and $N(CH_3)_3$ into cryogenic matrices was surprisingly low, product bands were nonetheless observed and reproducible. These were formed during twin jet deposition, where the only mixing of the two reagents takes place on the surface of the condensing matrix with very little available thermal energy. Many previous studies have shown that only the first intermediate in the reaction system is trapped under these conditions. In addition, the product bands that were detected grew upon annealing the matrices to between 25 and 35 K, indicating that the energy barrier to formation of the product is essentially zero. The fact that all of the primary product bands (see below for exceptions) grew at the same rate upon annealing and maintained a constant intensity ratio in different experiments with different reagent concentrations argues strongly for the formation of a single product species. The exceptions are the band at 2937 cm^{-1} in the H_2O_2/NH_3 system and the bands at 2916 and 3114 cm^{-1} in the H_2O_2/$N(CH_3)_3$ system. The 2937 and 2916 cm^{-1} bands did not grow on annealing, and had intensities that did not track with the remainder of the product bands from one experiment to the next. These bands are likely due to impurities, and certainly not to the primary product. The band at 3114 cm^{-1} appeared only upon annealing, and was relatively more intense at higher H_2O_2 concentration. The identity of the absorber responsible for this band will be discussed below.

The likely product in these two systems is a hydrogen-bonded complex between H_2O_2 and the base. This is consistent with the lack of an energy barrier to complex formation at 30 K, as noted above. Moreover, such complexes would be characterized principally by an O−H stretching band, ν_s, which is red-shifted and intensified relative to the H_2O_2 monomer.[35] The magnitude of the red shift can be estimated from the previous study of the H_2O_2:$O(CH_3)_2$ complex,[9] as well as from the ab initio calculations. The computed red shifts for H_2O_2:NH_3 and H_2O_2:$N(CH_3)_3$ are 400 and 683 cm^{-1}, respectively. The previous study of the H_2O_2:$O(CH_3)_2$ complex reported similar shifts. It should be noted that the computed shifts are gas-phase shifts, and many previous studies have shown that matrix shifts are larger than gas-phase shifts.[36] In addition, both experimental[14,16] and theoretical studies[17] have demonstrated that the shift of ν_s is greater in nitrogen matrices than in argon matrices, consistent with the observations here. The computed shifts are in agreement with the experimental shifts for the H_2O_2/NH_3 system of 351 and 424 cm^{-1} in Ar and N_2 matrices, respectively, and of 773 cm^{-1} for the H_2O_2/$N(CH_3)_3$ system in N_2. Moreover, corresponding bands appeared at significantly lower frequencies when D_2O_2 was substituted for H_2O_2, and the computed and experimental shifts of these bands are also in agreement. This provides additional support that these bands are associated with the hydrogen-bonded peroxide subunit in the complex. The experimental and computed band shifts for ν_s are summarized in Table 3.

An additional characteristic of these hydrogen-bonded complexes is a slight blue shift of the O−O−H bending motion involving the hydrogen-bonded hydrogen,[35] which is computed to be about +20 cm^{-1}. This bending mode occurs near 1280 cm^{-1} for parent H_2O_2. Weak bands shifted to around 1300 cm^{-1} were observed upon co-deposition with both bases, again arguing for the formation of a hydrogen-bonded complex.

All of these points taken together strongly support assignment of the primary product bands observed here and listed in Tables 1 and 2 to a hydrogen-bonded complex between H_2O_2 (or D_2O_2) and each of the two bases, with H_2O_2 serving as the proton donor. The stoichiometry of the complexes remains to be determined. However, the same product bands and hence the same product was observed over a wide range of concentrations, including experiments with very dilute concentrations. Further, except for the band at 3114 cm^{-1} in the H_2O_2/$N(CH_3)_3$ system, all of the bands appear to be associated with a single absorber. It is difficult to envision formation of a higher complex without initial formation of a 1:1 complex. Thus, it is very likely that the stoichiometry of the hydrogen-bonded complex is 1:1. The very good agreement of the band shifts computed for the 1:1 complexes and the experimental band shifts further supports this conclusion. Thus, the primary product observed in these experiments is assigned as the 1:1 hydrogen-bonded complex between H_2O_2 or D_2O_2 and a nitrogen base (NH_3 or $N(CH_3)_3$). The band at 3114 cm^{-1} in the H_2O_2/$N(CH_3)_3$ system appears only on annealing and is likely due to a complex of higher stoichiometry, possibly the 2:1 complex $(H_2O_2)_2$:$N(CH_3)_3$.

Band Assignments

Several of the band assignments have been discussed above, in the context of product identification. These assignments are collected in Tables 1 and 2. In addition, a distinct, sharp band for the H_2O_2:NH_3 complex was observed at 1051 cm^{-1} in solid argon and at 1066 cm^{-1} in solid nitrogen This band shifted strongly to lower energy when deuterated ammonia was employed, indicating that it is due to the base subunit in the complex. Many studies have demonstrated that ν_2, the symmetric deformation or bending mode of NH_3, shifts to higher energy upon complex formation, whether hydrogen bonded[11,16,37] or coordinated to a Lewis acid.[38,39] The magnitude of this shift is often taken as a measure of the strength of the interaction. On the basis of the shift of this mode from the parent band position near 970 cm^{-1} in similar hydrogen-bonded complexes, assignment of this mode to ν_2 is readily made. For the stronger proton donor HF, ν_2 for the FH:NH_3 complex was observed at 1094 cm^{-1} in solid argon,[13] a somewhat larger shift, as expected.

For the H_2O_2:$N(CD_3)_3$ complex, a weak doublet was observed near 1030 cm^{-1}, while a doublet was observed near 810 cm^{-1} for the D_2O_2:$N(CH_3)_3$ complex. A possible assignment for these doublets is to perturbed modes of the parent bases, which absorb near 1005 and 824 cm^{-1}, respectively (not the same mode for the two base isotopomers). The 1005 cm^{-1} band of $N(CD_3)_3$ has been assigned[40] to a CD_3 deformation mode, while the 824 cm^{-1} band of $N(CH_3)_3$ has been assigned to the NC_3 symmetric stretching mode. Both modes have been shown to be somewhat sensitive to complexation. The parent band at 1005 cm^{-1} for the H_2O_2:$N(CD_3)_3$ complex was computed to shift 29 cm^{-1} to higher energy, in good agreement with the experimental shift of +25 cm^{-1}. The parent band of $N(CH_3)_3$ at 824 cm^{-1} was computed to shift 5 cm^{-1} to lower energy. This is in the correct direction, although somewhat less than the experimental shift of 14 cm^{-1} to lower energy. For comparison, this base mode shifted 9 cm^{-1} to lower energy in the FH:$N(CH_3)_3$ complex.[41]

An alternative assignment might be to the librational mode of the H_2O_2 subunit moving with respect to the base subunit. For comparison, the librational mode of the FH:$N(CH_3)_3$ complex was observed at 1042 cm^{-1} in solid argon, rather near the present band position.[41] The librational mode is calculated to come at 984 cm^{-1} for the H_2O_2:$N(CD_3)_3$ complex, and at 699 cm^{-1} for the D_2O_2:$N(CH_3)_3$ complex. While in the same general region, these are not particularly close to the experimental band positions. Thus, the computations suggest assignment to perturbed modes of the base subunits in these complexes, although assignment to the librational mode cannot be ruled out. Also possible is assignment of the 1030 cm^{-1} doublet to the librational mode of HOOH:$N(CD_3)_3$ and assignment of the 810 cm^{-1} band to the perturbed NC_3 stretching mode of $N(CD_3)_3$ in the complex.

Product Yields

One unresolved question arising from the present study is the unexpectedly low yield of complex, as judged by the band intensities, particularly the intensity of the hydrogen-bond stretching mode ν_s. This mode is typically very intense and distinctive in hydrogen-bonded systems. In the previous study of the H_2O_2:$O(CH_3)_2$ complex, this band was quite intense and appeared even at very low reactant concentrations. Similar band intensities were observed for the 1:1 complexes of H_2O_2 with PH_3, $P(CH_3)_3$, and related bases.[42] In contrast, in the present study ν_s was weak, and not very readily identified, despite the fact that NH_3 and $N(CH_3)_3$ are stronger bases than $O(CH_3)_2$. The calculations indicate that the 1:1 complexes investigated in this work are quite strongly bound, and that the hydrogen-bond stretching mode should have a high absorption coefficient. Further, the calculations showed that there is no energy barrier to complex formation, a point verified by the growth of complex bands upon annealing. Thus, the apparent low yield of complex is puzzling. One possible explanation is that the full bandwidth of this band is very great, spreading the intensity over a wide energy range. That explanation is not particularly satisfying, in that it would have been surprising to see any band at all, yet a weak band was observed. This question remains under investigation.

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