The Peroxy Radical as Hydrogen Bond Donor and Hydrogen Bond Acceptor. A Matrix Isolation Study

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The interaction between the peroxy radical and water, hydrogen chloride, chlorine, and ammonia has been studied in argon matrixes. The peroxy radical acts as a hydrogen bond donor toward ammonia and forms a strong hydrogen bond to the ammonia nitrogen, significantly stronger than the corresponding water ammonia bond. Hydrogen chloride binds to the lone pair of the terminal oxygen of the peroxy radical, which in this case is a hydrogen bond acceptor. The complex shift of the hydrogen chloride stretch indicates a slightly weaker hydrogen bond than in the hydrogen chloride−water complex. The shift of the OH stretch of the complexed peroxy radical suggests the presence of a weak hydrogen bond from the peroxy radical hydrogen to one of the lone pairs of the chlorine atom of HCl. Water forms a cyclic complex with the peroxy radical, with both molecules donating and accepting hydrogen bonds. Both one water OH stretch and the OH stretch of the peroxy radical are strongly shifted in the complex. The results of this study suggest that the peroxy radical is a significantly stronger acid than water and that it readily accepts hydrogen bonds.

Introduction

The matrix isolation method was originally introduced for the study of unstable molecular species. As a test of the isolation properties of matrixes, Pimentel and co-workers studied the dimerization of water using infrared spectroscopy.[1] The combination of matrix isolation and infrared spectroscopy proved to be a very valuable tool for the study of molecular interactions. The absorption bands of matrix-isolated molecules are normally very sharp, making it easy to observe the shifted fundamentals of a complexed molecule in the presence of a large excess of the free molecule, and numerous studies of matrix isolated complexes between stable molecules have been published. After some initial difficulties had been solved, the first study of a free radical was published.[2] This study stimulated a strong intrest in free radical spectroscopy, and by now a large number of free radicals have been synthesized and studied with different spectroscopic methods in inert matrixes. In a few studies of matrix-isolated free radicals, evidence was obtained for the existence of interactions between the radical under investigation and some stable molecule trapped in the matrix. It seems logical to take advantage of the higher detection sensitivity now available with the FTIR method as compared to earlier grating IR studies and make a systematic study of complexes between radicals and small, stable molecules. The theoretical understanding of the factors governing the strength of complexes between stable molecules has matured in the past decade, and it is now possible to make fairly accurate predictions of energies of formation and intermolecular vibrations of complexes between stable molecules.[3] The interaction energy is mainly determined by electrostatic forces, and polarization and dispersion terms also make significant contributions. The relative weight of each of these terms will differ for radical−molecule complexes as compared to complexes between closed-shell molecules. It is therefore of interest to extend earlier studies of bimolecular complexes to radical−molecule complexes in order to see if the interaction potential model is valid also in theses cases.

The peroxy radical was first prepared by Milligan and Jacox,[4] and later a complete vibrational analysis was published by Smith and Andrews.[5] It plays an important role in the gas-phase chemistry of the atmosphere both in the troposphere and the stratosphere.[6] Its role in the chemistry of aerosol and cloud droplets is less clear. The partitioning of peroxy radicals between the gas phase and aerosol droplets is partially determined by its ability to accept and donate hydrogen bonds. The self-reaction of the peroxy radical makes it difficult to measure its equlibrium partitioning between the gas phase and aqueous media. Measurements of the uptake coefficient of the peroxy radical in water and sulfuric acid have been published,[7] but the reverse process, evaporation of peroxy radicals from liquid droplets, is probably very difficult to study. This paper presents an attempt to study the hydrogen bond donor and acceptor properties of the peroxy radical using the matrix IR method. One use of these data is to obtain data for intermolecular potential functions, which can be used in simulation programs to calculate Henry's law constants.

Experimental Section

Water was doubly distilled and degassed, and D_2O (Norsk Hydro 99.5% D) was degassed. An equlibrium mixture of H_2O and D_2O was used to obtain HDO. HCl was prepared from sulfuric acid and sodium chloride and degassed. Ammonia (Matheson lecture bottle) was degassed before use. The remaining gases, oxygen (AGA, 99.999%), $^{18}O_2$ (Isotech 97.3% ^{18}O), H_2 (AGA), D_2 (L′Air Liquide, N27), chlorine (AGA), and argon (L'Air Liquide 99.9995%), were used as received. Hydrogen peroxide was prepared from its urea complex (Aldrich 98%) as described in ref 8.

A cryostat, based on a Leybold closed cycle cooler RDK 10-320, was used in this work. It can operate between 10 and 100 K. The sample is condensed on a combined CsI−sapphire window, mounted in an OFHC copper frame. The temperature of the frame is measured with a Lake Shore silicon diode. The outer shroud of the cryostat can rotate relative to the frame, allowing different windows to be aligned with the frame. The outer shroud has a pair of CsI windows for infrared transmission

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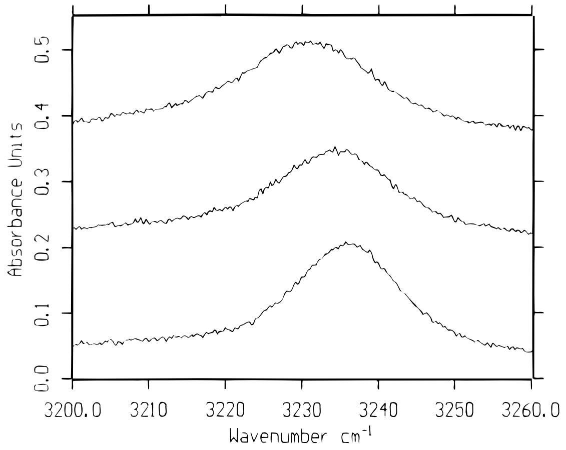

Figure 1. The OH stretching vibration of HOO bound to H_2O (bottom), HDO (middle), and D_2O (top). The curves have been shifted vertically for clarity.

TABLE 1: Observed Bands of the Peroxy−Water Complex (cm^{-1})

	HOO[a]	HOO−HOH	HOO−DOH	HOO−DOD
ν_1	3413.0	3236.2	3234.4	3230.6
ν_2	1388.9	1479.3	1481.0	1482.2
ν_3	1100.8	1120.4	1120.4	1120.4
$2\nu_2$		2875		2875
		2858		2862
		2833		2837

	DOO[a]	DOO−HOH	DOO−HDO	DOO−DOD
ν_1	2530.2	2396.4	2393.8	2390.3
ν_2	1020.3	1085.0	1085.0	1085.0
ν_3	1122.9	1127.9	1127.9	1127.9
$2\nu_2$		2154.1	2150	2144.7

	HOH[b]	HOH−OOH
ν_1	3638.0	3501.5
ν_3	3734.3	3691

[a] Reference 12. [b] Reference 13.

spectroscopy, and a pair of sapphire windows for UV−vis spectroscopy. A blade valve allows the use of different sample preparation devices together with the cryostat. A window on the shroud, opposite the inlet valve, allows for the irradiation of the sample during deposition. Another window in the same vertical plane as the CsI windows and with a 45° entrance angle makes it possible to irradiate the matrix during the recording of an IR spectrum. The matrixes were deposited and spectra recorded at 17K. Infrared spectra were recorded at 0.5 cm^{-1} resolution between 450 and 4000 cm^{-1} using a Bruker 113v FTIR.

Peroxy radicals were synthesized on the growing matrix surface by the addition of hydrogen atoms to molecular oxygen. Three different sources of hydrogen atoms were used: molecular hydrogen, water, and hydrogen chloride. Argon mixed with 1−2% of the hydrogen atom precursor was passed through a microwave discharge before entering the cryostat, while argon mixed with ca. 2% oxygen and varying amounts of ammonia, water, or hydrogen chloride entered the cryostat through a separate channel.

DOO experiments were carried out with deuterium gas, D_2O, or HDO as deuterium atom sources.

In a few experiments, $^{18}O_2$ was used instead of natural oxygen in order to investigate the source of water in experiments with H_2 or D_2 as atom sources.

Assignment

Nomenclature. In complexes of the type studied here, the intramolecular vibrations of the complex components retain their original character in the complex. Therefore, the perturbed *i*th fundamental of A in a complex with B will be denoted as ν_i(A−B). When the isotopic composition of B is immaterial, water will be denoted as Aq and the peroxy radical as perox.

HOO−H_2O. As reported by Smith and Andrews,[5] hydrogen atoms add to molecular oxygen on the matrix surface to produce peroxy radicals in high yield.

A broad, intense peak at 3236.2 cm^{-1} is observed when HOO and H_2O are simultaneously present in an argon matrix, regardless of the source of the hydrogen atoms used to prepare HOO. When D_2O and HOO are present the peak shifts to 3230.6 cm^{-1} (Figure 1), and with DOO instead of HOO, corresponding peaks appear in the 2390 region (Table 1). The intensity of the band correlates with the water concentration as expected for a 1:1 complex. The intensity of the 3236 cm^{-1} band correlates with the strength of the bands of free HOO, and it is far too strong to be due to anything but a species with one HOO. The band at 3236.2 cm^{-1} is therefore assigned to ν_1(OOH−OH_2), the OH stretch of HOO complexed with H_2O. The large shift from the OH stretch of free HOO, 176.8 cm^{-1}, shows that HOO is hydrogen bonded to the water oxygen. In addition to the 3236 or 2390 cm^{-1} bands, sets of weaker bands appear, whose intensities are a constant fraction of the OH or OD intensities. With HOO, bands are observed at 1120.4 cm^{-1} and near 1480 cm^{-1}. The position of the 1120.4 cm^{-1} band is independent of the isotopomer of water used and is assigned to ν_3(OOH−Aq), the OO stretch of complexed HOO. The 1480 cm^{-1} band shifts slightly toward higher wavenumbers when D_2O is used instead of H_2O. A band at 1479.3 cm^{-1} is assigned to ν_2(OOH−OH_2) and a band at 1482.2 cm^{-1} to ν_2(OOH−OD_2). The large shift from 1388.9 cm^{-1} in free HOO to 1480 cm^{-1} in complexed HOO is typical for a OH bend of a hydrogen bond donor. The corresponding bands of complexed DOO have also been observed; see Table 1. In addition to these bands, which are due to shifted peroxy radical fundamentals, water induced a set of peaks in the interval 2875−2833 cm^{-1} with HOO and at approximately 2150 cm^{-1} with DOO. The precise positions of the peaks depend on the water isotopomer used (Table 1). The DOO bands coincide with CO−water bands, however the CO-water bands are sharp and the DOO−Aq bands are broad and relatively intense so there is no difficulty in differentiating between the bands. (A small amount of CO is formed in the microwave discharge.) The intensities of the bands in the 2800 and 2150 cm^{-1} regions are constant fractions of the intensities of the OH or OD stretches of complexed HOO or DOO and they are therefore assigned to the 1:1 complexes OOH−Aq and OOD−Aq, respectively. For HOO, the position of this band is near the expected position of $2\nu_2$(OOH−Aq). Using the calculated band positions of ref 9, one can estimate the anharmonicity of the bend in free HOO. If the result is scaled to take care of the complex shift using the Darling Dennison prescription,[10] the position of the bend overtone of complexed HOO is estimated to 2923 cm^{-1}, 48 cm^{-1} above the observed band. The bending overtone is therefore expected to be red shifted by 48 cm^{-1} by a Fermi resonance with the OH stretch. This implies the presence of a coupling term in the vibration Hamiltonian of the order of 100 cm^{-1} between the HOO bend and the OH stretch. The situation for the complexed DOO radical is a little more complicated since in DOO the bend and the OO stretch are strongly coupled. The frequency of the 2150

TABLE 2: Observed Bands of the Peroxy Radical Complexes with Hydrogen Chloride and Chlorine (cm^{-1})

	HOO[a]	HOO−HCl	HOO−ClCl
ν_1	3413.0	3306.0	3335.0
ν_2	1388.9	1425.2	1408.0
ν_3	1100.8	1117.0	1110.6
	DOO[a]	DOO−HCl	DOO−ClCl
ν_1	2530.2	2450.8	2473.5
ν_2	1020.3	1053.4	1038.4
ν_3	1122.9		
	HCl[b]	ClH−OOH	ClH−OOD
	2870.8	2677.4	2682.0
		ClCl[c]	ClCl−OOH
		549	546

[a] Reference 12. [b] Reference 14. [c] Reference 15.

TABLE 3: Observed Bands of the Peroxy Radical−Ammonia Complex (cm^{-1})

	HOO[a]	DOO[a]	NH$_3$[b]	OOH−NH$_3$	OOD-NH$_3$
ν_1	3413.0	2530.2		2654.2	2049.0
ν_2	1388.9	1020.3		1563	
ν_3	1100.8	1122.9		1126.8	
ν_2			966.9	1087.4	1086.2
ν_{lib}				804.3	617.4

[a] Reference 12. [b] Reference 16.

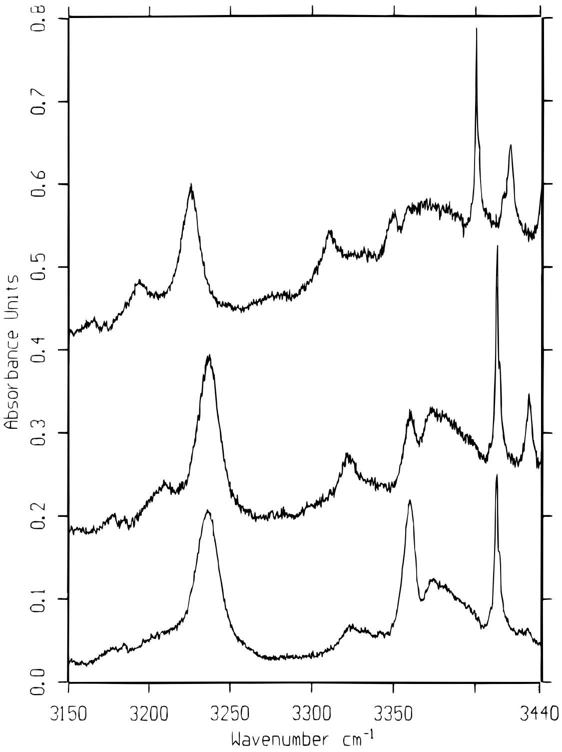

Figure 2. Part of the OH stretching region in different experiments. Upper curve: H + $^{18}O_2$ with H_2 as hydrogen atom source. Middle curve: H + $^{16}O_2$ with H_2 as hydrogen atom source and with H_2O introduced together with O_2 (Ar:H_2O, 1:252). Lower curve: H + $^{16}O_2$ with H_2O as hydrogen atom source and with H_2O introduced together with O_2 (Ar:H_2O, 1:139). The broad, strong band in the left-hand part of the spectrum is ν_1(OOH−OH$_2$); the strong, sharp band in the right-hand part of the spectrum is ν_1(HOO). The curves have been shifted vertically for clarity.

cm^{-1} band is approximately twice the frequency of the OO stretch and DOO bend at 1127.9 and 1085.0 cm^{-1}. The 2150 cm^{-1} band is therefore probably an overtone of one of these bands in Fermi resonance with the strong OD stretch of complexed DOO.

With H_2O a band is observed at 3501.5 cm^{-1} when peroxy radicals are present. The band position is independent of the isotopic composition of the radical. The position of the band is close to but clearly below the water trimer band, when no D_2O or HDO is present in the matrix. Its intensity varies as expected for a 1:1 complex, and it is assigned to ν_1(HOH−perox). A weak band at 3691 cm^{-1} is tentatively assigned to ν_3(HOH−perox). ν_1(DOD−perox) and ν_1(HOD−perox) are expected in the OD stretching region of the water trimer. This region is quite complicated,[11] but two bands at 2572 and 2586 cm^{-1} seem to be too intense in some experiments to be due to trimer isotopomers.

HOO−HCl. Experiments were carried out with H_2O and HCl as hydrogen atom sources and with D_2O as a deuterium atom source. A set of bands appeared which were only present when both peroxy radicals and hydrogen chloride were simultaneously present in the matrix. The bands appeared to have constant intensity ratios and reasonable isotope shifts. They were preliminarily assigned to the hydrogen chloride peroxy radical complex. With HCl as the hydrogen atom source, bands of a molecular chlorine peroxy radical complex also appeared. Its bands were identified in a separate experiment, were molecular chorine was added to the argon oxygen gas mixture. The assignment is collected in Table 2.

HOO−NH$_3$. Experiments were performed with H_2O and H_2 as hydrogen atom sources and with D_2 as deuterium source. The effect of hydrogen atoms on ammonia was tested in a separate experiment, with the oxgen left out. No reaction products were observed. A set of bands were preliminarily assigned to an ammonia peroxy radical complex on the basis of their constant intensity ratios and reasonable isotope shifts. The assignment is collected in Table 3.

Discussion

The bands assigned to the peroxy radical−water complex are summarized in Table 1. They appear in a constant intensity ratio regardless of the hydrogen atom source used. With a given hydrogen atom source one observes additional sets of bands, which correlate reasonably well with the peroxy radical−water bands. For instance, when one uses water as a hydrogen atom source, one gets a relatively large ozone concentration in the matrix, and the ozone water complex has a set of fairly strong bands,[17] which in these experiments correlate with the peroxy−water bands. The bands of the water−ozone complex are absent, or very weak, when molecular hydrogen is used as hydrogen atom source. Figure 2 illustrates the difference between hydrogen and water as hydrogen atom sources. Note that the gas-phase reaction between oxygen atoms and hydroxyl radicals to form molecular oxygen and atomic hydrogen is very fast and the formation of HOO is relatively slow at the pressure of the deposition line, so the argon−water discharge produces mainly hydrogen atoms and oxygen atoms in addition to undissociated water. The hydrogen and oxygen atoms from the discharge add to molecular oxygen on the matrix surface to produce peroxy radicals and ozone, respectively.

With molecular hydrogen as the hydrogen atom source, relatively large amounts of hydrogen peroxide are formed. The yield of hydrogen peroxide is much smaller relative to the peroxy−water complex when water is the hydrogen atom source. Separate experiments were carried out with hydrogen peroxide and water to eliminate the possibility that the assigned bands were due to hydrogen peroxide complexes. Experiments were also performed with hydrogen atoms from discharged molecular hydrogen and hydrogen peroxide; no reaction products were observed.

In addition to forming hydrogen peroxide, the reaction between hydrogen atoms and peroxy radicals produces water and oxygen atoms. This reaction path was first noted in an experiment, in which D_2 mixed with argon was used as a D atom source, and argon mixed with oxygen and H_2O entered the cryostat through the second channel. The matrix thus formed contained, in addition to the directly introduced H_2O, a significant amount of D_2O but practically no HDO. Separate experiments showed that H atoms do not attack D_2O and D atoms do not attack H_2O. No reaction was expected, since both H_3O and $H_2 + OH$ are less stable than $H_2O + H$ by more than 10 kcal/mol.[18] To study the reaction between H atoms and O_2 further, H atoms were added to $^{18}O_2$. In addition to the expected $H^{18}O^{18}O$ and $H^{18}O^{18}OH$, a significant amount of $H_2{}^{18}O$ was formed but only a trace of ozone. The water$-^{18}$O spectrum was very similar to the spectrum of a matrix where the water had been introduced the normal way as a mixture with argon. Most of the water was present as rotating monomer, and the major dimer bands were clearly visible. The vibration−rotation bands were rather broad and in a few cases shifted by a wavenumber from their normal positions. The results were confirmed by an experiment where D atoms were added to $^{18}O_2$. Since no oxygen atom−water complex was observed, this means that the newly formed water molecule and oxygen atom are normally separated by at last one layer of argon atoms after the reaction. The enthalpy of reaction for

$$H + HOO \rightarrow H_2O + O$$

is approximately 53 kcal/mol,[19] so the water and oxygen atom formed have enough energy to separate. The oxygen atom from this reaction may be expected to react with molecular oxygen in the matrix to form ozone. However this is not observed. Perhaps hydrogen atoms from the discharge penetrate several atomic layers into the growing argon matrix to react with already formed peroxy radicals. Molecular oxygen appears to fit extremely well into the argon lattice and may be protected from reaction as soon as it is covered by a single layer of argon atoms. A peroxy radical and a peroxy radical−water complex are too big to fit into a single substitutional site of the argon matrix. They may therefore perturb the matrix to make it easier for a hydrogen atom to approach and react. The oxygen atom set free in the reaction between a peroxy radical and a hydrogen atom takes a little more than half the reaction enthalpy. This is sufficient to separate from the water molecule but probably not enough to get out of the perturbed matrix surrounding it.

The strongly red-shifted OH stretch and the blue-shifted bend of the peroxy radical−water complex and the red-shifted OH stretch of the complexed water (Table 1) indicate that both the peroxy radical and the water molecule donate hydrogen bonds. Therefore the complex must have a cyclic structure with the peroxy radical donating a hydrogen bond to the water oxygen and water in turn forming a hydrogen bond with the end oxygen of the peroxy radical. From molecular models of water and the peroxy radical, and the assumption of hydrogen bond lengths of the same size as in the water dimer, this structure is only slightly more strained than that of the water trimer.

The strongly shifted HCl stretch of hydrogen chloride (Table 2) complexed to a peroxy radical shows that HCl forms a hydrogen bond to the peroxy radical. Given the charge distribution of the peroxy radical it is likely to bind to the end oxygen. The complex shifts of the peroxy radical are significantly smaller than the corresponding shifts of peroxy radicals bound to water (Table 1) or ammonia (Table 3) but larger than those of the peroxy radical complexed to chlorine (Table 2). The shifts may indicate a weak hydrogen bond from the peroxy radical to hydrogen chloride. The structure of such a cyclic complex should not be more strained than the structures of the $(H_2O)_2HCl$ and $H_2O(HCl)_2$ complexes, which are cyclic.[14]

Chlorine may be expected to act as an electron acceptor and bind to a lone pair on the end oxygen of the peroxy radical. Compared to the shifts one normally sees in non-hydrogen-bonded complexes between closed shell molecules, the OH shift of the peroxy radical complexed to chlorine is large. With the peroxy radical, there is as yet not sufficient experience to tell wether this shift is due to a weak hydrogen bond from the peroxy radical to chlorine or to its larger polarizability due to the unpaired electron. It seems possible that the chlorine−peroxy radical complex has a cyclic structure with chlorine binding to the end oxygen of the peroxy radical, which in turn forms a weak hydrogen bond to chlorine.

The bands assigned to the peroxy radical−ammonia complex clearly show that the peroxy radical forms a strong hydrogen bond to the ammonia nitrogen. The 759 cm^{-1} red shift of the OH stretch of the peroxy radical and the 120 cm^{-1} blue shift of the ammonia out-of-plane bend are clear indicators of a strong hydrogen bond interaction. The new strong band at 804.3 cm^{-1} must be an intermolecular fundamental. Its large H to D shift shows that it is due to a hydrogen atom motion, and in analogy with water complexes[20] it is expected to be due to a libration of the complexed peroxy radical around its O−O bond. Its high value also points to a strong complex. Unfortunately the NH stretching region of ammonia is complex and it is not clear if there is a weak hydrogen bond from ammonia to the peroxy radical.

For hydrogen chloride complexes, there seems to be a general correlation between complex strength and the shift of the HCl stretching frequency.[21] The HCl stretching frequency in the peroxy radical complex, 2677.4 cm^{-1}, is only slightly less shifted than the corresponding frequency of the water complex, 2664.0 cm^{-1}, indicating that the complexes are similar in strength. The peroxy radical−hydrogen chloride complex may have a small additional contribution from a weak hydrogen bond from the peroxy radical to the chlorine atom. Latajka and Scheiner give the dissociation energy of the water−hydrogen chloride complex at 0 K as −3.3 kcal/mol.[22] We may therefore estimate the corresponding dissociation energy of the peroxy radical−hydrogen chloride complex as lying between −3 and −4 kcal/mol depending on the possible contribution from the OOH−ClH bond.

The shift of the symmetric bending vibration of ammonia complexed with a peroxy radical is quite large, 120.5 cm^{-1}. It is thus almost as large as in the HF−ammonia complex, 126.6 cm^{-1},[23] and much larger than in the water−ammonia complex, 68.5 cm^{-1}.[24] For the HF−ammonia complex, Latajka and Scheiner calculated an electronic contribution to the dissociation energy of −15.13 kcal/mol,[25] which can be corrected for zero point vibration energy using frequencies given in ref 26 to give a 0 K dissociation energy of −12.1 kcal/mol. For the ammonia−water complex, the dissociation energy at 0 K is estimated to lie between −3.3 and −4 kcal/mol using electronic energies and frequencies given in refs 3, 27, and 28. The correlation between the complex shift of the out-of-plane bend of ammonia and the dissociation energy of the complex is very approximate. There are unknown contributions to the shift of the ammonia bend and to the dissociation energy of the complex from a possible hydrogen bond from ammonia to the peroxy radical end oxygen. Given these uncertainties, it seems reasonable to estimate a dissociation energy between −6 and −12 kcal/mol for the peroxy radical−ammonia complex from the figures given above. For water complexes, it has been found that the frequency of the out-of-plane shear vibration of the complexed water correlates with the square root of the dissociation energy.[20] The intermolecular libration of the complexed peroxy radical has the same form as the out-of-plane shear vibration of complexed water, since the Eckard conditions force the complexed water to librate around the free OH bond, while the complexed peroxy radical librates around the OO bond. The out-of-plane shear vibration of water bound to ammonia is 638 cm^{-1}.[3] Using the estimates for the ammonia−water dissociation energy given above and the libration frequency of the peroxy radical−ammonia complex, one gets an estimated dissociation energy of −5 to −6 kcal/mol. Unfortunately it is not possible to give a more precice estimate at present, but it seems clear that the peroxy radical is a significantly stronger hydrogen bond donor than water.

The complex shift of the water OH stretch involved in the hydrogen bond to the peroxy radical is of the same order as that found for water complexes with dimethyl ether and acetone,[3] and one may therefore expect a contribution to the dissociation energy of between −3 and − 4 kcal/mol from this hydrogen bond. From the comparison between the ammonia−peroxy radical complex and the water−ammonia complex, one expects that the contribution from the peroxy radical−water hydrogen bond to the dissociation energy is larger than the dissociation energy of the water dimer, −2.8 kcal/mol.[3] The dissociation energy of the peroxy radical−water complex is therefore likely to be at least −6 kcal/mol. Note that the observed shift of the OH stretch of the peroxy radical bound to water, 176.8 cm^{-1}, is lowered by approximately 50 cm^{-1} due to a Fermi resonance with the HOO bend overtone.

The results of this paper suggest that the peroxy radical is a significantly stronger acid than water and that it readily accepts hydrogen bonds. It can therefore be expected to dissolve very readily in water. A more detailed study of the hydrogen-bonding properties of the peroxy radical requires measurements of the intermolecular vibrations of radical molecule complexes in combination with model calculations along the lines of ref 3. The results of this work suggests that such a study is feasible, and we hope to begin this work soon.

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