New Radical−Molecule Association Compounds

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Abstract: The formation of two new association species, hydroperoxy−formic acid and hydroperoxy−acetic acid, are examined. These species have especially large binding energies of 12.8 and 18.6 kcal mol^{-1}, respectively. Because of this, the lifetime of the species with respect to thermal decomposition is found to be long. The chemical implications of such new species are discussed.

I. Introduction

Association species are known to form in the atmosphere.[1] An association species will typically exist in equilibrium with the reactants that form it.

$$A + B + M \rightleftarrows AB + M \qquad (1)$$

In many cases, this equilibrium is strongly temperature-dependent, with formation of products being favored at lower temperatures. Lifetimes of these species are longer at cold temperatures. The result is that these associated species act as reservoirs for the reactants that form them. At colder temperatures, these reservoirs can be transported and thermally decompose back into their parent reactants in warmer regions. This leads to the possibility of species being transported to remote regions of the atmosphere, where their number densities would not be expected to be so large. Examples of this are peroxyacetyl nitrate (PAN)[2,3] and pernitric acid (PNA).[4−7] PAN is thought to be formed predominately in polluted air, but found in remote regions of the atmosphere.[8−11] Due to the high stability of PAN, it can transport its reactants, peroxyacetyl radical and nitrogen dioxide, over long distances. These classic association species involve the formation of two radical species held together by weak covalent bonding.

In this work, we report a new class of association species involving cyclic radical−molecule complexes that are held together by strong hydrogen bonding. While molecular complexes are known to exist in the atmosphere, they are generally weakly bound, and hence relatively short-lived. Two such complexes have been identified: hydroperoxyl−formic acid and hydroperoxyl−acetic acid. On the basis of extensive ab initio computational studies of these complexes, we assess whether these complexes exist and where they could be spectroscopically identified. Moreover, on the basis of an analysis of the equilibrium constant and lifetime of these species, we consider the possibility of their formation in the atmosphere. These complexes approach the stability of species with known atmospheric significance, such as PNA and PAN. Furthermore, these calculations demonstrate that organic acid complexes may act as precursors to organic aerosols, similar to sulfuric and nitric acid.

Formic acid and acetic acid are both present in the atmosphere. Typical concentrations of these species are 500 to 1000 parts per trillion (ppt) in remote areas, with acetic acid generally present in twice the concentrations of formic acid.[12,13] Latitudinal and longitudinal studies clearly indicate an anthropogenic influence on the concentration of these organic acids. Polluted atmospheric concentrations of formic acid of 10 ppb have been measured.[14] Gas-phase formation of acetic acid is thought to occur via reaction of peroxyacetyl radical with the hydroperoxyl radical (HO_2).[15] Removal of these organic acids from the atmosphere occurs via rain out or reaction with the hydroxyl radical. Interestingly, these organic acids have been found to account for a larger fraction of the acidity in remote areas than in urban areas, where sulfuric and nitric acid account for most of the acidity.[16] Moreover, researchers have found that water forms relatively strong complexes with both formic and acetic acids. Rablen et al.[17] report binding energies (D_o) of 7.0 kcal mol^{-1} for both of these complexes. Formic acid dimer is thought to be unreactive toward OH.[18] Wine et al.[19] have suggested that, in the atmosphere, the formic acid−water complex is formed

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and its reactivity with OH is lowered. A recent publication of jet-cooled formic acid−water complex includes rotational spectra and calculations for that species.[20]

II. Computational Methods

All high-level density functional theory calculations were performed using the GAUSSIAN 94[21] suite of programs. Geometries were optimized using the Becke three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation [B3LYP][22] method. This method has been shown to produce reliable results for hydrogen-bonded complexes when compared with other methods.[23,24] Work in this laboratory on the HO_2-H_2O complex[25] has shown that his method yields similar results to more computationally expensive methods when examining these types of complexes. The 6-311++G(3df,3pd) basis set was used[26−29] for geometry optimizations, energy calculations, and frequency calculations. Calculations were also done using medium and other large basis sets to ensure that there was convergence within these parameters. Only global minima are reported in this study, but other conformations of the molecules in this work were explored. The zero-point correction energy calculated at this level of theory for all molecules was used when computing D_o at all levels of theory. Zero-point energies taken from these frequency calculations can be assumed to be an upper limit due to the anharmonic nature of the potential energy surface. Using the data from our calculations, it is possible to calculate relevant thermodynamic properties of the formation of these complexes. Room-temperature data for the monomers were taken from NASA's JPL Publication 97-4[1]. These data were extrapolated to other temperatures in methods similar to other works done in laboratory.[30] The dissociation constants (k_{diss}) for the complex have also been calculated using a method first developed by Troe,[31,32] and further shown to be effective by Patrick and Golden[33] for reactions of atmospheric importance. From this, we calculate the lifetimes of these species. The thermodynamic data for the products of the reactions forming the complexes can be calculated from the data obtained in the ab initio calculations. Room-temperature data for the reactants were taken from NASA's JPL Publication 97-4[1]. These data were extrapolated to other temperatures using Kirchhoff's law:

$$\Delta H(T_2) - \Delta H(T_1) = \Delta C_p \Delta T \tag{2}$$

where T is the temperature and ΔC_p is the difference in heat capacity at constant pressure of the substances whose enthalpy is being calculated to those of the elements in their natural state. Differences in heat capacities were assumed to be independent of temperature. Entropies were extrapolated to different temperatures using the following equation:

$$S(T_2) - S(T_1) = C_v \ln(T_2/T_1) \tag{3}$$

where C_v is the heat capacity at constant volume.

III. Results and Discussion

A. Structure. The structure and geometry for hydroperoxyl−formic acid (HO_2-HCO_2H) are shown in Figure 1, top. There are two hydrogen bonds labeled R1 and R2. The shorter one (R1), between the hydrogen on the hydroperoxyl radical (H_3) and the carbonyl oxygen on the formic acid (O_2), has a length of 1.639 Å. The longer one (R2), between the hydroxyl hydrogen on the formic acid (H_1) and the terminal oxygen on the hydroperoxyl radical (O_4), has a length of 1.724 Å. These are both much shorter than typical hydrogen bond distances for the water dimer (∼1.95 Å) and in HCO_2H-H_2O (1.786 Å). The geometry of the atoms in $HO_2-HC(O)OH$ is significantly different from those in isolated HO_2 and HC(O)OH. The hydrogen−oxygen bond distance of the hydroperoxyl radical (H_3-O_3) is lengthened by 3.7% relative to isolated HO_2. On the formic acid, the bond distances H_1-O_1 and $C-O_2$ are 3.2% and 1.8% longer than in isolated HC(O)OH. As a result of this, $C-O_1$ is shortened by 2.5% relative to formic acid. The fully optimized geometry of the hydroperoxyl−formic acid complex is given in Table 1.

The structure and geometry of the hydroperoxyl−acetic acid is shown in Figure 1, bottom. As can be seen, it has the same configuration as hydroperoxyl−formic acid, except a methyl group is substituted for a hydrogen opposite the hydroxyl group. The H_5-O_2 hydrogen bond (R1) is shorter than in $HO_2-HC(O)OH$ by 0.03 Å, while the H_1-O_4 hydrogen bond (R2) is longer than the analogous bond in hydroperoxyl−formic acid by 0.008 Å. As a result of a shorter R1, the H−O bond distance on the hydroperoxyl radical (H_5-O_3) is elongated by 4.1% in hydroperoxyl−acetic acid. As was the case for the hydroperoxyl−formic acid, the carbon−oxygen double bond (C_1-O_2) and the oxygen−hydrogen bond (H_1-O_1) on the acetic acid are both longer than those in isolated $CH_3C(O)OH$. In this case, C_1-O_2 is elongated by 2.4% and H_1-O_1 is elongated by 3.4% relative to the monomer. The carbon−oxygen single bond (C_1-O_1) and carbon−carbon bond (C_1-C_2) on acetic acid are shortened by 3.1% and 0.9%, respectively. The perturbation to the monomer geometry is greater than was the case for hydroperoxyl−formic acid, indicating a stronger interaction in hydroperoxyl−acetic acid. The fully optimized geometry for hydroperoxyl−acetic acid is given in Table 2.

B. Vibrational Frequencies. Vibrational frequencies and rotational constants for these species were also calculated. Rotational constants for the species studied in this work were calculated to provide information for laboratory identification of them, and are listed in Table 3. In all of these complexes, modes that are present in the parent molecules are present in the associated species. These modes are often shifted and their band strengths altered with respect to the same modes in the parent molecules. The magnitude of the shift is often an indication of the strength of the interaction between the associated species parent molecules. There are also new modes unique to the associated species. Strong intermolecular interactions cause the vibrational modes common to the associated species and the isolated parent species to be quite perturbed in this case. In the hydroperoxyl−formic acid complex, elongation of the H_3-O_3 coordinate leads to a 652 cm^{-1} red-shift in the O−H stretching frequency on the hydroperoxyl relative to isolated HO_2. Furthermore, this band is predicted to have a band intensity that is 14 times stronger than in the isolated hydro-

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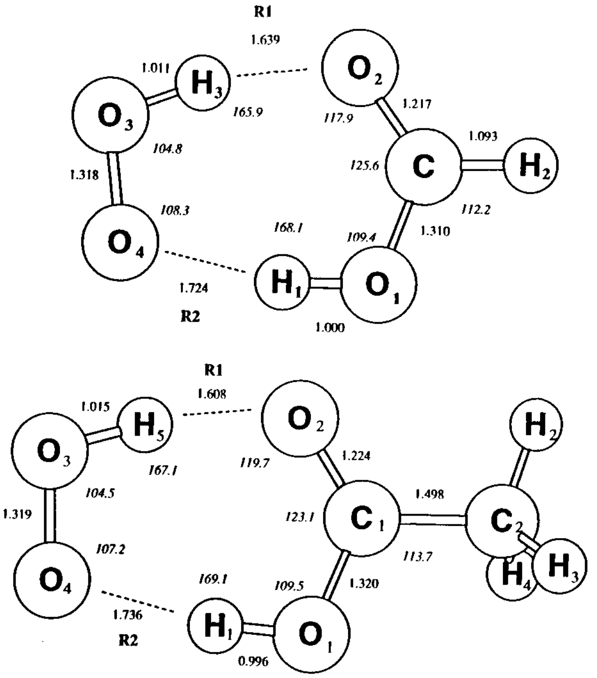

Figure 1. Frame 1 (top): Structure and Geometry of hydroperoxyl−formic acid. Frame 2 (bottom): Structure and geometry of hydroperoxyl−acetic acid.

Table 1. Geometry of Hydroperoxyl−Formic Acid

B3LYP/6-311++G(3df,3pd)					
distances[a]		angles[b]		dihedrals[b]	
R1	1.639	$O_3H_3O_2$	165.9	$O_4O_3H_3O_2$	−0.2
R2	1.724	$O_4H_1O_1$	168.1	$H_1O_1CO_2$	0.0
H_3O_3	1.011	$H_3O_3O_4$	104.8	$H_1O_1CH_2$	180.0
O_3O_4	1.318	H_1O_1C	109.4	$O_1CO_2H_3$	0.0
H_1O_1	1.000	O_1CO_2	125.6	$O_1H_1O_4O_3$	0.1
CO_1	1.310	O_1CH_2	112.1		
CO_2	1.217				
CH_2	1.093				

[a] All bond distances are given in angstroms. [b] Bond angles and dihedrals are given in degrees.

Table 2. Geometry of Hydroperoxyl−Acetic Acid

B3LYP/6-311++G(3df,3pd)					
distances[a]		angles[b]		dihedrals[b]	
R1	1.608	$O_3H_5O_2$	167.1	$O_4O_3H_5O_2$	0.9
R2	1.736	$O_4H_1O_1$	169.2	$O_3O_4H_1O_1$	−0.4
H_5O_3	1.015	$H_5O_3O_4$	104.4	$H_5O_2C_1O_1$	−0.1
O_3O_4	1.319	$H_1O_1C_1$	109.5	$H_1O_1C_1O_2$	0.1
H_1O_1	0.996	$O_1C_1O_2$	123.1	$O_1C_1C_2H_2$	180.0
C_1O_1	1.320	$O_2C_1C_2$	113.7	$O_1C_1C_2H_3$	−58.3
C_1O_2	1.224	$C_1C_2H_2$	110.1	$O_1C_1C_2H_4$	59.1
C_1C_2	1.498	$C_1C_2H_3$	109.5	$O_2C_1C_2H_2$	0.4
C_2H_2	1.084	$C_1C_2H_4$	109.6		
C_2H_3	1.090				
C_2H_4	1.090				

[a] All bond distances are given in angstroms. [b] Bond angles and dihedrals are given in degrees.

peroxyl radical. On the formic acid, the O−H stretch is red-shifted by 554 cm^{-1}, with an intensity that is 24 times greater than that of isolated formic acid.

The same mode in the formic acid−water complex is red-shifted by 389 cm^{-1}, reflecting the weaker interaction in that molecule. Besides being an indicator of the strength of intermolecular interaction, these shifts provide a means for identification of the species using infrared spectroscopy. With shifts from isolated species in the hundreds of wavenumbers, these modes are displaced significantly from the absorptions of their parent monomers, thus allowing for spectral identification of these species. Intermolecular modes are unique to the associated species and provide a further source for positive identification of the species. More strongly bound complexes will have modes that are higher in energy due to shorter intermolecular distances. Hydroperoxyl−formic acid has a stretching mode along the R1 coordinate that has a calculated frequency of 849 cm^{-1} and an intensity of 144.7 km mol^{-1}. Along with the shifted modes, this mode is a good candidate for spectral identification of HO_2−HC(O)OH. Formic acid dimer has similarly shifted modes,[34,35] making spectral isolation of HO_2−HC(O)OH more complicated. The calculated vibrational frequencies for formic acid−water and the hydroperoxyl formic acid complex are listed in Table 4.

Table 3. Rotational Constants of the Species Studied

rotational const[a]	species			
	HC(O)OH−H_2O	HO_2−HC(O)OH	CH_3C(O)OH−H_2O	HO_2−CH_3C(O)OH
A	11849	8993	11054	8543
B	4959	3268	2607	1820
C	3520	2397	2146	1514

[a] All rotational constants are reported in MHz.

In hydroperoxyl−acetic acid, the O−H stretch on the hydroperoxyl radical is red-shifted 713 cm^{-1} relative to isolated HO_2. The intensity of that mode is 28 times greater in the complex than in the monomer. This red-shift is larger than the analogous shift in hydroperoxyl−formic acid by 61 cm^{-1}. This reflects the larger change in geometry along this coordinate, as well as the stronger interaction in hydroperoxyl−acetic acid. The acetic acid modes are shifted in a similar pattern as was seen for hydroperoxyl−formic acid. As one might expect, acetic acid dimer also has[34,36] a similar pattern of shifts as the complexes studied here. The O−H stretch is shifted by 596 cm^{-1}, 42 cm^{-1} more than in HO_2−HC(O)OH. This mode is calculated to be 33 times more strongly absorbing than in acetic acid. The same mode in the acetic acid−water complex has a calculated red-shift of 578 cm^{-1}. As was the case for hydroperoxyl−formic acid, the intermolecular stretching mode along the R1 coordinate has a relatively high energy vibrational frequency at 877 cm^{-1}, with an intensity of 151.3 km mol^{-1}. All the vibrational frequencies for hydroperoxyl−acetic acid and acetic acid water are listed in Table 5.

C. Binding Energies. The binding energies (D_o) and well depths (D_e) of the species studied in this work have also been calculated and are listed in Table 6. Hydroperoxyl−acetic acid has a well depth of 21.0 kcal mol^{-1}, and a binding energy of 18.6 kcal mol^{-1}. This is tremendous, considering that the water dimer[37−40] has a well depth of about 4.8 kcal mol^{-1}. Typically, hydrogen bond interactions have energies of 2−7 kcal mol^{-1} and are thought to involve essentially linear arrangements of donors and proton acceptors.[41,42] In this case, the hydrogen

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Table 4. Vibrational Frequencies for Hydroperoxyl−Formic Acid and Formic Acid Water[a]

	formic acid−water				hydroperoxyl−formic acid			
mode description	freq	intensity	shift	factor	freq	intensity	shift	factor
H_2O								
H−O−H asymmetric stretch	3874	87.3	−39	1.5				
H−O−H symmetric stretch	3654	274.4	−160	61				
H−O−H bend	1625	120.5	−2	1.7				
HO_2								
O−H stretch					2950	344.2	−652	14
H−O−O bend					1620	150.3	+184	3.8
O−O stretch					1227	11.8	0	0.43
formic acid								
O−H stretch	3346	590.0	−389	9.9	3181	1434.0	−554	24
C−H stretch	3053	72.6	0	76	3088	161.1	+35	4.0
C═O stretch	1773	334.7	−46	0.90	1736	292.8	−83	0.79
H−C−O bend	1387	15.2	−16	6.6	1395	17.7	−8	7.7
H−O−C bend	1453	1.7	+154	0.19	1470	2.4	+171	0.27
C−O stretch	1213	225.2	+90	0.86	1253	177.1	+130	0.67
H_2 out-of-plane wag	1069	7.3	+17	4.3	1079	12.2	+27	7.2
H_1 out-of-plane wag	932	118.0	+260	0.85	974	49.4	+302	0.36
O−C−O bend	703	48.3	+72	1.1	713	22.7	+82	0.53
unique modes	618	155.0			849	144.7		
	371	69.5			336	77.0		
	285	97.3			246	3.9		
	217	31.0			236	1.2		
	193	36.0			199	4.1		
	174	13.4			111	1.2		

[a] Vibrational frequencies and shifts are reported in cm^{-1}. Intensities are reported in km mol^{-1}. Factor is the intensity of the associated species (listed) divided by the intensity of the isolated monomer.

Table 5. Vibrational Frequencies for Hydroperoxyl−Acetic Acid and Acetic Acid Water[a]

	acetic acid−water				hydroperoxyl−acetic acid			
mode description	freq	intensity	shift	factor	freq	intensity	shift	factor
H_2O								
asymmetric stretch	3791	59.5	−122	1.0				
symmetric stretch	3536	379.2	−278	84				
H−O−H bend	1726	105.0	+99	1.5				
HO_2								
O−H stretch					2889	692.8	−713	28
H−O−O bend					1630	202.4	+194	5.1
O−O stretch					1226	10	+57	0.36
acetic acid								
O−H stretch	3232	610	−578	13	3214	1520.4	−596	33
C−H stretch	3185	12.6	+28	3.7	3166	14.8	+9	4.4
C−H stretch	3134	5.6	+40	0.95	3113	1.7	+19	0.29
C−H stretch	3072	1.5	+35	0.33	3056	5.7	+19	1.3
C═O stretch	1800	280.4	−54	0.92	1738	265	−116	0.87
H−C−H bend	1512	17.6	+23	2.3	1481	28.8	−8	3.8
H−C−H bend	1505	8.5	+32	1.2	1478	9	+5	1.2
C−C stretch	1492	14.7	+93	0.36	1463	31.5	+64	0.77
C−O−H bend	1333	229.2	+40	0.59	1329	197.7	+36	0.51
C−O stretch	1423	53.1	+223	13	1404	36.5	+204	8.9
CH_3 torsion	1071	11.4	−10	2.2	1076	8.9	+12	1.8
CH_3 torsion	1034	22.8	+46	1.9	1032	20.2	+44	1.7
C−C−O bend	900	9.5	+44	0.31	907	2.1	+51	0.07
H−O−C═O torsion	632	10.7	+31	7.6	640	29.4	+39	21
C−C═O bend	598	2.2	−2	0.33	603	0.3	+3	0.05
H_1 out-of-plane wag	989	125.3	+512	1.3	962	31.3	+485	0.32
O═C−O bend	451	33.1	+18	8.7	468	31.1	+35	8.2
CH_3 twist	99	4.2	−3	7.0	98	0.4	−4	0.67
unique modes	776	360.3			877	151.3		
	387	80.4			317	52.9		
	337	91.3			224	2.7		
	234	17.1			179	6.6		
	208	19.6			116	0.3		
	64	2.1			58	0.7		

[a] Vibrational frequencies and shifts are reported in cm^{-1}. Intensities are reported in km mol^{-1}. Factor is the intensity of the associated species (listed) divided by the intensity of the isolated monomer.

bound complex has a cyclic arrangement due to the formation of two hydrogen bonds. Each monomer acts as a hydrogen donor and an acceptor. This is similar to what is seen in the formic and acetic acid dimers. The binding energies of these dimers have been measured[43] to be between 12 and 15 kcal mol^{-1}. Even a strong acid−water complex that is cyclic, such as nitric acid−water,[44] has a well depth of 9.5 kcal mol^{-1} and a binding energy of 7.2 kcal mol^{-1}. Of the species we present here, only formic acid−water, which has a D_o of 9.6 kcal mol^{-1} and a D_e of 7.0 kcal mol^{-1}, is similar to those numbers. This is in good agreement with the energies calculated by Rablen et al.[17]

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Table 6. Thermodynamic and Kinetic Data

	formic acid−water	hydroperoxyl−formic acid	acetic acid−water	hydroperoxyl−acetic acid
D_e	9.6	15.2	14.7	21.0
D_o	7.0	12.8	11.7	18.6
$\Delta H_f(300)$	−155.0	−100.0	−172.3	−118.5
$\Delta H_f(200)$	−154.0	−99.3	−170.7	−116.9
$S°(300)$	73.4	77.3	81.3	86.9
$S°(200)$	66.2	70.1	72.1	77.5
$K_f(300)$	4.1×10^{-22}	6.1×10^{-19}	8.7×10^{-19}	2.0×10^{-13}
$K_f(200)$	3.8×10^{-19}	8.4×10^{-14}	2.8×10^{-13}	1.8×10^{-5}
$k_{diss}(300)$	5.3×10^{-12}	1.4×10^{-14}	2.1×10^{-13}	1.4×10^{-16}
$k_{diss}(200)$	3.4×10^{-14}	7.6×10^{-19}	4.4×10^{-17}	1.1×10^{-22}
A	4.8×10^{-28}	3.2×10^{-29}	8.7×10^{-30}	2.4×10^{-29}
B	4100	7100	7600	11000
a	1.3×10^{-7}	4.8×10^{-6}	4.8×10^{-6}	2.3×10^{-4}
b	−3030	−5890	−5080	−8430

[a] Binding energy (D_o), well depth (D_e), and enthalpy of formation are reported in kcal mol^{-1}. Gas-phase entropy data are reported in cal mol^{-1} K^{-1}. Formation constant (K_f) is reported in cm^3 molecule^{-1}. Dissociation rate constant (k_{diss}) is reported in molecule cm^{-3} s^{-1}.

Hydroperoxyl−formic acid has a binding energy that is less than that of hydroperoxyl−acetic acid, 12.8 kcal mol^{-1}. We have also calculated the enthalpies of formation and gas-phase entropies of the species in this study at 300 and 200 K.

D. Atmospheric Implications. We use these data to determine the equilibrium constants for the formation (K_f) of these species from their parent monomers. This equilibrium constant is for reaction 1, where AB is the associated species, M is the collision partner, and A and B are the parent monomers. Hydroperoxyl−acetic acid has the most favorable K_f of the species examined in this study, with an equilibrium constant of formation of 2.0×10^{-13} cm^3 molecule^{-1} at 300 K. At 200 K, K_f increases by nearly 8 orders of magnitude to 1.8×10^{-5} cm^3 molecule^{-1}. This is nearly as large as the equilibrium constants for the formation of pernitric acid [$K_f(300) = 1.6 \times 10^{-11}$, $K_f(200) = 1.0 \times 10^{-3}$]. The equilibrium constant for the formation of hydroperoxyl−formic acid is much smaller than this, 6.1×10^{-19} and 8.4×10^{-14} cm^3 molecule^{-1} at 300 and 200 K, but is still relatively large. It is larger than K_f for the formation of nitrogen dioxide dimer (N_2O_4), [$K_f(300) = 2.5 \times 10^{-19}$, $K_f(200) = 1.4 \times 10^{-14}$],[1] for instance. These data can be fit to a general equation, as is done in ref 1, for a temperature-dependent equilibrium constant, $K_f(T)$.

$$K_f(T) = A \exp(B/T) \tag{4}$$

A and B are constants related to the thermodynamic data in Table 6. Under reasonable urban conditions[12] the number densities of the carboxylic acids can be 2.6×10^{11} molecule cm^{-3}, and for hydroperoxyl radical 2.6×10^{8} molecule cm^{-3}. With a temperature of 283 K, the equilibrium number density of hydroperoxyl−acetic acid would be about 8×10^{7} molecule cm^{-3}.

The dissociation rate constants for the thermal decomposition of these species at 300 and 200 K are presented in Table 6, as well. The dissociation rate constant (k_{diss}) for the thermal decomposition of these associated species (eq 1) can be quite slow compared to that for other complexes. For hydroperoxyl−acetic acid, k_{diss} is 1.4×10^{-16} cm^3 molecule^{-1} s^{-1} at 300 K, and 1.1×10^{-22} cm^3 molecule^{-1} s^{-1} at 200 K. The dissociation rate constants for hydroperoxyl−formic acid are larger, 1.4×10^{-14} cm^3 molecule^{-1} s^{-1} at 300 K and 7.6×10^{-19} cm^3 molecule^{-1} s^{-1} at 200 K. Just as we did for the equilibrium constants, we fit our output to a general equation for a temperature-dependent dissociation constant, $k_{diss}(T)$.

$$k_{diss} = a \exp(b/T) \tag{5}$$

The constants for this and the equilibrium general formula are given in Table 6. Using these data, we can calculate lifetimes for these species in the atmosphere. Hydroperoxyl−acetic acid will have the longest lifetime of these species. At the surface, at a temperature of 283 K, k_{diss} will be 2.7×10^{-17} cm^3 molecule^{-1} s^{-1}. With a typical total number density of 2.6×10^{19} molecule cm^3, the lifetime of $HO_2{-}CH_3C(O)OH$ will be short, about 1.4 ms. However, in the upper troposphere, where number densities are lower and temperatures are colder, this lifetime will increase. At 18 km, reasonable number densities and temperatures are 2.7×10^{18} molecule cm^3 and 210 K. Under these conditions, the lifetime of hydroperoxyl−acetic acid will be 7.6 min. Also, at these low temperatures, equilibrium toward the formation of the species will be most favored.

IV. Conclusions

The hydroperoxyl radical−acetic acid and hydroperoxyl radical−formic acid complexes constitute a rare example of strong hydrogen bonding that is of the magnitude of weak covalently bonded systems. Leopold et al.[45] have coined systems similar to these as partially bonded molecules. This results in significant changes in the way we think of the chemistry of organic acids. In addition to contemplation of processes involving the isolated molecule, chemical and photochemical processes including the complex must also be considered. Furthermore, the role of these complexes as precursors to organic aerosols must also be examined. The fact that the binding energies of these complexes are larger than those of strong acids substantiates that organic acids may play roles similar to nitric and sulfuric acid in aerosol formation.

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