Water Complexation as a Means of Stabilizing the Metastable HO$_3$ Radical

**Simone Aloisio and Joseph S. Francisco***

Contribution from the Department of Chemistry and Department of Earth and Atmospheric Sciences, Purdue University, West Lafayette, Indiana 47907

Received March 29, 1999. Revised Manuscript Received June 9, 1999

Abstract: The metastable intermediate HO$_3$ is found to be stabilized by formation of a complex with water. We have calculated the geometry and energy of the HO$_3$–H$_2$O complex, which is 6.5 kcal mol^{-1} lower in energy than isolated HO$_3$ and H$_2$O.

I. Introduction

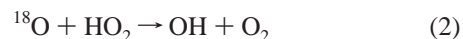The reaction

$$H + O_3 \rightarrow OH + O_2 \qquad (1)$$
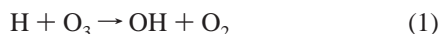
is an important reaction in the study of atmospheric chemistry. It has been the topic of many experimental[1–10] and theoretical[11–17] studies. Both have produced evidence that the reaction goes through a metastable intermediate, HO$_3$; but no studies have reported the isolation or characterization of HO$_3$.

The question of whether HO$_3$ is stable enough to be isolated has been the subject of some debate in the literature. Even in the most recent studies,[13,15–17] a wide range of stabilities with respect to the products of reaction 1 (OH and O$_2$) have been reported. Mathison et al.[13] state that the HO$_3$ minimum is 27.2 kcal mol^{-1} above the products using their computed SCF data with no electron correlation. Dupuis et al.[15] calculate that HO$_3$ is 13.8 kcal mol^{-1} below OH and O$_2$ using Multi-Configuration Hartree–Fock (MCHF) methods. Vincent and Hillier[16] then used Quadratic Configuration Interaction methods including singles and doubles (QCISD) to optimize geometries, then adding triples

[QCISD(T)] to obtain energies. They calculated that HO$_3$ is 1.2 kcal mol^{-1} above the products of reaction 1. A recent study by Jungkamp and Seinfeld[18] predicts HO$_3$ to be 1.15 kcal mol^{-1} more stable than OH and O$_2$. They also calculate the heat of formation (ΔH_f^{298}) of HO$_3$ to be 6.1 kcal mol^{-1}. Most recently, Varandas and Yu[17] used Unrestricted Configuration Interaction methods including singles and doubles (UCISD) to calculate HO$_3$ as being 0.5 kcal mol^{-1} more stable than OH and O$_2$, and ΔH_f^{298} to be 11.6 kcal mol^{-1}. Speranza[19] studied hydrogen trioxide ion (HO$_3^+$) using Fourier Transform Ion Cyclotron Resonance (FT-ICR) spectrometry, and from that data, measured a ΔH_f^{298} for HO$_3$ of -1 ± 5 kcal mol^{-1}.

Sridharan et al.[20] showed that a metastable HO$_3$ intermediate is involved in the reaction,

$$^{18}O + HO_2 \rightarrow OH + O_2 \qquad (2)$$

through an elegant laser induced fluorescence (LIF) experiment. By isotopic labeling of the oxygen atom, they were able to determine whether reaction 2 went through a simple hydrogen abstraction or if it proceeded through the HO$_3$ intermediate. The simple hydrogen abstraction path would yield ^{18}OH as the primary product. This was not found to be the case. In fact, large signals for ^{16}OH were observed, signaling that the reaction must go through the HO$_3$ intermediate. A detailed theoretical study of the reaction dynamics and kinetics of reaction 2 has been published by Wang and co-workers.[21]

In this work, we explore the possibility of stabilizing HO$_3$ through the formation of a complex with water. The reaction for this formation is given below.

$$HO_3 + H_2O \rightarrow HO_3\text{–}H_2O \qquad (3)$$
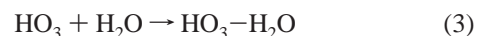
Due to the small difference in energy between HO$_3$ and its dissociation products, the concept we put forward is that water complexation may provide a stabilizing effect for the HO$_3$ radical.

(1) Clyne, M. A. A.; Monkhouse P. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 298–309.

(2) Lee, J. H.; Michael, J. V.; Payne, W. A., Jr.; Stief, J. *J. Chem. Phys.* **1978**, *69*, 350–353.

(3) Keyser, L. F. *J. Phys. Chem.* **1979**, *83*, 645–648.

(4) Finlayson-Pitts, B. J.; Kleindiest, T. E. *J. Chem. Phys.* **1979**, *70*, 4804–4806.

(5) Howard, C. J.; Finlayson-Pitts, B. J. *J. Chem. Phys.* **1980**, *72*, 3842–3843.

(6) Washida, N.; Akimoto, H.; Okuda, M. *J. Chem. Phys.* **1980**, *72*, 5781–5783.

(7) Finlayson-Pitts, B. J.; Kleindiest, T. E.; Ezell, J. J.; Toohey, D. W. *J. Chem. Phys.* **1980**, *74*, 4533–4543.

(8) Washida, N.; Akimoto, H.; Okuda, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3496–3503.

(9) Force, A. P.; Wiesenfeld, J. R. *J. Chem. Phys.* **1981**, *70*, 1718–1723.

(10) Dodonov, A. F.; Zelenov, V. V.; Kukui, A. S.; Tal'Rose, E. A. P. V. L. *Khim. Fiz.* **1985**, *4*, 1335–1343.

(11) Blint, R. J.; Newton, M. D. *J. Chem. Phys.* **1973**, *59*, 6220.

(12) Chen, M. M. L.; Wetmore, R. W.; Schaefer, H. F., III *J. Chem. Phys.* **1981**, *74*, 2938.

(13) Mathisen, K. B.; Gropen, O.; Kamcke, P. N. S.; Wehlgren, U. *Acta Chem. Scand. A* **1983**, *37*, 817–822.

(14) Mathisen, K. B.; Siegbahn, P. M. *Chem. Phys.* **1984**, *90*, 225.

(15) Dupuis, M.; Fitzgerald, G.; Lester, W. A., Jr.; Schaefer, H. F., III *J. Chem. Phys.* **1986**, *85*, 2691–2697.

(16) Vincent, M. A.; Hillier, I. H. *J. Phys. Chem* **1995**, *99*, 3109–3113.

(17) Verandas, A. J. C.; Yu, H. G. *Mol. Phys.* **1997**, *91*, 301–318.

(18) Jungkamp, T. P. W.; Seinfeld, J. H. *Chem. Phys. Lett.* **1996**, *257*, 15–22.

(19) Speranza, M. *Inorg. Chem.* **1996**, *35*, 6140–6151.

(20) Sridharan, U. C.; Klein, F. S.; Kaufman, F. *J. Chem. Phys.* **1985**, *82*, 592–593.

(21) Wang; W.; González-Jonte, R.; Varandas, A. J. C. *J. Phys. Chem* **1998**, *102*, 6935–6941.

Table 1. Optimized Geometries for HO_3

		B3LYP				
species	coordinate[a]	6-31G(d)	6-311++G(d,p)	6-311++G(2d,2p)	6-311++G(2df,2p)	6-311++G(3df,3pd)
trans HO_3	HO′	0.979	0.972	0.971	0.971	0.970
	O′O″	1.541	1.565	1.549	1.545	1.543
	O″O‴	1.246	1.230	1.235	1.232	1.230
	HO′O″	97.5	98.4	98.4	98.6	98.6
	O′O″O‴	110.1	110.5	110.2	110.3	110.2
	HO′O″O‴	180.0	180.0	180.0	180.0	180.0
cis HO_3	HO′	0.982	0.975	0.974	0.973	0.973
	O′O″	1.504	1.519	1.508	1.504	1.502
	O′O‴	1.261	1.248	1.252	1.249	1.247
	HO′O″	98.8	100.3	99.8	100.0	99.9
	O′O″O‴	112.2	113.0	112.7	112.8	112.7
	HO′O″O‴	0.0	0.0	0.0	0.0	0.0

[a] All bond distances are given in angstroms. All angles and dihedrals are given in degrees.
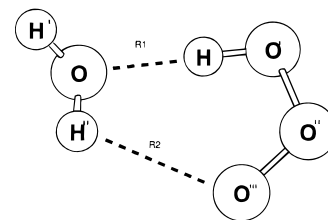
II. Computational Methods

All calculations were performed using the GAUSSIAN 94[22] suite of programs. Geometries were optimized using the Becke three-parameter hybrid functional combined with the Lee, Yang, and Parr correlation [B3LYP][23] density functional theory method. This method has been shown to produce reliable results for hydrogen-bonded complexes when compared with other methods.[24−26] Basis sets employed are 6-31G(d), 6-311++G (d,p), 6-311++G (2d,2p), 6-311++G-(2df,2p), and 6-311++G (3df,3pd). Frequency calculations were also performed at this level 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. Furthermore, single-point energies using the optimized geometries were calculated using Coupled Cluster theory including singles, doubles, and triples [CCSD-(T)][27] using all basis sets but the largest one.

III. Results and Discussion

A. Geometry and Vibrational Frequencies. We have found two stable geometries for the HO_3 molecule. Both are planar, one in a cis and the other in a trans configuration. The geometries for these isomers is listed in Table 1. Other researchers[11,13,15,17] have optimized a more stable isomer in which the hydrogen atom is out of plane with respect to the three oxygen atoms. This configuration was not found to be a minimum in our calculations. The equilibrium geometry we have calculated is in good agreement with the previous calculations of Vincent and Hillier,[16] which predict a planar minimum. Those researchers used levels of theory as high as QCISD(T)/6-311++G(2d,p) in their calculations.

For the HO_3−H_2O complex, an optimized structure was obtained consisting of a six-membered ring of the HO_3 molecule and an O−H of the water molecule. The remaining H atom is out of plane with respect to the ring. This is shown in Figure 1. The primary interaction is between the O (hydrogen acceptor) on the water and the H (hydrogen donor) on the HO_3. The bond distance between these two atoms is calculated to be 1.782 Å

(22) GAUSSIAN 94, Revision D.2; Frisch, M. J.; Trucks, G. W.; Schlegel, H. G.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; GAUSSIAN, Inc.: Pittsburgh, PA, 1995.
(23) Becke, A. M. *J. Chem. Phys.* **1993**, *98*, 5648.
(24) Kim, K.; Jordan, K. D. *J. Phys. Chem.* **1994**, *98*, 10089−10094.
(25) Bene, J. E.; Person, W. B.; Szczepaniak, K. *J. Phys. Chem.* **1995**, *99*, 10705−10707.
(26) Novoa, J. J.; Sosa, C. *J. Phys. Chem.* **1995**, *99*, 1583715845.
(27) Raghavachari, K.; Trucks. G. W.; Pople. J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

Figure 1. The structure of HO_3−H_2O.

at the B3LYP/6-311++G(3df,3pd) level of theory. We can compare this to other HO_x complexes with water. Xie and Schaefer[28] have found that OH makes a bimolecular complex with water in which the hydroxyl radical is the hydrogen donor and the water the hydrogen acceptor. The intermolecular bond distance they found was calculated to be 1.94 Å. In our laboratory,[29] we have calculated a structure for an HO_2−H_2O complex that has a similar ring structure as HO_3−H_2O. In that case, the hydroperoxyl hydrogen donor-to-water bond distance was calculated to be 1.781 Å. This is virtually identical with the HO_3−H_2O complex. There also may be a weak interaction between the terminal oxygen of HO_3 and the in-plane hydrogen atom of water. The distance between these atoms is 2.475 Å. By contrast, in HO_2−H_2O the distance between the terminal oxygen of HO_2 and the in-plane hydrogen atom of water is 2.406 Å. The HO_3, when complexed with water, is in the cis configuration. Just as in the isolated HO_3, when complexed, the bond between the terminal O and the middle O is shorter than the bond between the O bonded to hydrogen and the middle bond. It should be noted, however, that the O″−O‴ bond is slightly longer in the HO_3−H_2O complex than in the isolated HO_3, while the O′−O″ bond is slightly shorter. The geometry for HO_3−H_2O is listed in Table 2.

The rotational constants for the isolated parent monomers, as well as those for the HO_3−H_2O complex, are shown in Table 3. It can be seen that HO_3−H_2O is an asymmetric rotor since $A \neq B \neq C$. It is almost an oblate top since $A \neq B \approx C$ (11600, 4269, and 3148 respectively) and $A > B$. This is consistent with a six-membered ring and out-of-plane hydrogen structure shown in Figure 1.

The HO_3−H_2O complex has nine intramolecular vibrational modes that are common to those of the isolated parent monomers (six from HO_3 and three from H_2O). There are an additional six intermolecular modes unique to the complex. The calculated band centers and band strengths of these modes are listed in Table 4, along with the same information for the isolated monomers. The nine vibrational modes with the largest frequen-

(28) Xie, Y.; Schaefer, H. F., III *J. Chem. Phys.* **1993**, *94*, 2057.
(29) Aloisio, S.; Francisco, J. S. *J. Phys. Chem* **1998**, *102*, 1899−1902.

Table 2. Optimized Geometry for HO_3-H_2O

	B3LYP				
coordinate[a]	6-31G(d)	6-311++G(d,p)	6-311++(2d,2p)	6-311++(2df,2p)	6-311++(3df,3pd)
R1	1.738	1.780	1.794	1.786	1.782
R2	2.226	2.548	2.596	2.488	2.475
H'O	0.974	0.965	0.963	0.962	0.964
H''O	0.971	0.963	0.962	0.964	0.962
HO'	1.005	0.992	0.990	0.991	0.991
O'O''	1.471	1.487	1.478	1.474	1.472
O''O'''	1.276	1.262	1.264	1.262	1.260
H'OH''	104.3	106.6	106.1	106.4	106.2
H'OH	90.5	103.1	100.0	98.3	97.3
OHO'	174.0	176.4	179.6	177.3	177.9
HO'O''	102.4	102.7	102.5	102.5	102.5
O'O''O'''	114.5	114.2	113.9	114.0	114.0
O''O'''H'	114.1	114.7	113.7	114.2	114.4
O'''H'O	122.0	107.4	108.7	112.0	112.9
HO'O''O'''	-1.6	-12.9	-9.6	-13.5	-9.8
H'OHO'	21.7	-1.9	113.1	3.9	7.6
H''OHO'	-83.6	-124.5	-2.1	-111.3	-121.5
OHO'O''	-8.3	10.2	-108.5	5.0	12.0

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

Table 3. Rotational Constants[1] for HO_3-H_2O and HO_3

		B3LYP				
species		6-31G(d)	6-311++G(d,p)	6-311++G(2d,2p)	6-31++G(2df,2p)	6-311++G(3df,3pd)
HO_3-H_2O	A	11274	11414	11589	11518	11600
	B	4609	4266	4146	4272	4269
	C	3309	3132	3080	3149	3148
trans HO_3	A	73764	74816	74609	75059	75115
	B	11098	10934	11077	11129	11161
	C	9646	9540	9645	9692	9717
cis HO_3	A	67934	69505	69102	69556	69688
	B	11672	11494	11625	11672	11702
	C	9961	9863	9951	9994	10020

[a] Rotational Constants are given in MHz.

cies are assigned to the intramolecular modes, while the intermolecular modes are the remaining six. There are some significant shifts in the intramolecular modes with respect to the same modes in the isolated parent monomers. We choose to compare the frequencies in the complex to the cis isomer of HO_3, since it most resembles the configuration of HO_3 in the complex. An examination of the structure in Figure 1 suggests that the most affected modes would be the ones involving the H atom on the HO_3 because the interaction with the water molecule would be greatest there. This is indeed the case. The H–O' stretch is shifted to the red by 342 cm^{-1} relative to isolated HO_3. This is larger than the equivalent shifts for HO_2-H_2O[26] and $HO-H_2O$,[25] which are 296 and 99 cm^{-1} to the red, respectively. The band strength of this mode is also increased by a factor of 13.3. This is due to the increase in the dipole moment that is induced by this mode with the addition of the water. The mode that is most shifted however is the H–O'–O'' wag. This mode is predicted to be shifted by 481 cm^{-1} to the blue. The H–O'–O' bend is also predicted to be blue shifted by 100 cm^{-1}. Other moderate shifts are in the O'–O''–O''' symmetric and asymmetric stretches, which are shifted 59 and 52 cm^{-1} to the blue, respectively. The magnitudes of these shifts are testament to the strength of the interaction between the H_2O and HO_3 molecules in the complex.

B. Relative Energies. We have calculated the energies of the two HO_3 isomers using density functional theory (B3LYP). We have also taken the geometries calculated by this method and calculated a single-point energy using coupled cluster theory [CCSD(T)]. These calculations are presented in Table 5. The B3LYP full optimization with the 6-311++G(3df,3pd) basis

set predicts that the trans isomer is more stable than the cis isomer by 0.2 kcal mol^{-1}. This is in general agreement with Mathisen et al.[13] and their calculation of a more stable trans isomer. The CCSD(T) single-point calculation of the same geometry with the same bass set predicts the cis isomer to be more stable by 0.7 kcal mol^{-1}, however. This agrees with Vincent and Hillier[16] and Varandas and Yu[17] in predicting a more stable cis isomer. The main message from all these calculations is that HO_3 is very weakly bound. Moreover, it is unlikely to be seen directly in experimental studies of reaction 1 or 2.

We find that the addition of water to form an HO_3-H_2O complex stabilizes the HO_3. The binding energies for this complex are shown in Table 6. We compare the energy of the complex to the cis isomer of HO_3 because the configuration of HO_3 in the complex is cis. The B3LYP/6-311++G(3df,3pd) optimization predicts a binding energy (D_o) of 4.9 kcal mol^{-1}, while the CCSD(T)/6-311++G(2df,2p) single point predicts a binding energy of 6.5 kcal mol^{-1}. HO_3-H_2O is more weakly bound than HO_2-H_2O, which has a D_o calculated to be 6.2 kcal mol^{-1} at the B3LYP/6-311++G(3df,3pd) optimization. It is more strongly bound than $HO-H_2O$, which has a calculated D_e of 5.6 kcal mol^{-1}, compared to 7.0 kcal mol^{-1} for HO_3-H_2O at the B3LYP/6-311++G(3df,3pd) level of theory. Other researchers[17] have found the nonplanar global minimum for HO_3 to be about 0.5 kcal mol^{-1} lower in energy than either of the two isomers calculated in this work. The binding energies calculated for the complex stated above are an order of magnitude larger than that. We therefore think that water will indeed stabilize HO_3.

Table 4. Vibrational Frequencies[a,b] for HO_3 and HO_3-H_2O

| | | | B3LYP | | | | | | | | | |
| | | | 6-31G(d) | | 6-311++G(d,p) | | 6-311++G(2d,2p) | | 6-311++G2df,2pd | | 6-311++G(3df,3pd) | |
species	mode no.	mode description	freq	intensity	freq	intensity	freq	intensity	freq	intensity	freq	intensity
trans HO₃	1	HO′ st	3674	43.0	3741	75.5	3744	75.3	3742	75.1	3741	70.3
	2	HO′O″ bend	1403	4.1	1380	38.9	1384	19.0	1385	20.3	1390	22.4
	3	O″O‴ st	1257	134.9	1225	137.3	1241	140.5	1239	139.3	1240	135.9
	4	O′O″O‴ sym st	693	58.2	626	49.5	654	64.8	659	67.6	659	64.1
	5	O′O″O‴ asym st	479	43.7	431	87.4	452	75.0	459	73.8	461	75.6
	6	HO′O″ wag	199	120.4	166	129.2	171	113.8	178	113.7	186	108.7
cis HO₃	1	HO′ st	3620	33.9	3680	52.5	3691	53.5	3688	52.9	3686	49.3
	2	HO′O″ bend	1437	65.3	1391	72.6	1414	70.4	1412	70.2	1412	72.4
	3	O″O‴ st	1256	8.9	1228	16.5	1238	15.7	1237	14.4	1240	12.1
	4	O′O″O‴ sym st	736	124.4	689	151.1	709	151.8	715	154.9	714	150.1
	5	O′O″O‴ asym st	479	9.1	433	27.2	456	20.0	461	19.3	461	19.0
	6	HO′O″ wag	292	119.5	179	131.3	233	114.0	227	114.6	231	106.2
HO₃−H₂O	1	H′OH″ asym st	3813	73.3	3906	97.0	3900	94.7	3898	97.9	3888	95.4
	2	H′OH″ sym st	3696	29.2	3799	21.0	3799	17.6	3792	19.8	3785	17.6
	3	HO′ st	3224	629.2	3364	655.1	3366	673.1	3358	663.5	3344	657.3
	4	H′OH″ bend	1713	72.9	1613	86.2	1640	84.6	1631	82.0	1624	82.3
	5	HO′O″ bend	1555	63.2	1498	60.8	1511	62	1511	58.5	1512	60.7
	6	O″O‴ st	1243	17.8	1229	28.3	1238	26	1239	25.0	1242	23.1
	7	O′O″O‴ sym st	809	111.7	748	143.5	766	138.9	771	138.0	733	133.6
	8	HO′O″ wag	788	122.0	679	167.2	700	128.4	702	125.9	712	115.0
	9	O′O″O‴ asym st	549	149.7	486	21.0	503	18.8	509	18.4	513	18.7
	10	HOH′ bend	497	137.3	380	89.8	379	91.1	389	108.7	394	96.3
	11	HOH″ bend	296	90.0	256	160.3	267	147.0	265	136.2	273	138.5
	12	H″OHO′ torsion	254	11.1	213	16.3	203	11.9	207	14.9	208	16.1
	13	H′OHO′ torsion	172	61.9	168	54.1	142	53.4	161	56.0	165	54.5
	14	OH′O′ bend	148	29.7	92	9.3	74	9.7	93	9.6	94	11.1
	15	OHO′O″ torsion	63	1.1	34	2.1	49	2.9	55	2.1	53	2.0

[a] All frequencies are reported in cm^{-1}. [b] All intensities are reported in $km\ mol^{-1}$.

Table 5. Relative Energy of Cis and Trans HO_3 Isomers[a]

| | ΔE[d] | |
basis set	B3LYP[b]	CCSD(T)[c]
6-31G(d)	−0.7	−0.2
6-311++G(d,p)	0.9	1.7
6-311++G(2d,2p)	0.1	−0.6
6-311++G(2df,2p)	0.2	1.0
6-311++G(3df,3pd)	0.2	−0.7

[a] $\Delta E = [E(\text{cis } HO_3) - E(\text{trans } HO_3)]$. [b] From full optimization. [c] Single point using B3LYP optimized geometry with the same basis set. [d] All of the energy differences include the differences in zero-point energies.

Table 6. Binding Energies ($kcal\ mol^{-1}$) of the HO_3-H_2O Complex

| | B3LYP[a] | | CCSD(T)[b] | |
basis set	D_e	D_o	D_e	D_o
6-31G(d)	11.6	9.1	10.1	7.6
6-311++G(d,p)	8.1	5.9	8.4	6.2
6-311++G(2d,2p)	7.1	5.1	7.7	5.7
6-311++G(2df,2p)	6.5	5.0	8.0	6.5
6-311++G(3df,3pd)	7.0	4.9		

[a] From full optimization. [b] Single point using B3LYP optimized geometry of the same basis set.

Thermodynamic data for the formation of HO_3-H_2O are given in Table 7. The values for water at room temperature were taken from NASA's JPL Publication 97-4.[30] For HO_3 and HO_3-H_2O, ΔH_f^0 was taken from the calculated difference in their internal energies and the published data for OH and O_2 in ref 30. These data were extrapolated to other

(30) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling*, Evaluation No.12; National Aeronautics and Space Administration-Jet Propulsion Laboratory: Pasadena, 1997.

Table 7. Thermodynamic Data[a−c]

| | species | | | | species | | |
	HO₃−H₂O	HO₃	H₂O		HO₃−H₂O	HO₃	H₂O
ΔH_f^0	−53.2	11.9	−57.1	ΔS^{200}	73.6	59.0	42.6
ΔH_f^{200}	−53.7	11.5	−57.6	ΔS^{300}	81.6	63.1	45.1
ΔH_f^{300}	−54.0	11.3	−57.8	K_f^{200}	4.8×10^{-18}		
				K_f^{300}	1.8×10^{-20}		

[a] Enthalpy values are given in $kcal\ mol^{-1}$. [b] Entropy values are given in $cal\ mol^{-1}\ K^{-1}$. [c] Formation constants are given in $cm^3\ molecule^{-1}$.

temperatures using Kirchhoff's law:

$$\Delta H(T_2) - \Delta H(T_1) = \Delta C_p \Delta T \qquad (4)$$

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. The heat capacities and entropies for all the species at 298 K were taken from the output of the ab initio calculations. Differences in heat capacities were assumed to be independent of temperature. Entropies were extrapolated to different temperatures using the following equation:

$$S(T_2) - S(T_1) = C_v \ln(T_2/T_1) \qquad (5)$$

where C_v is the heat capacity at constant volume. At 300 K, HO_3-H_2O has an enthalpy of formation (ΔH_f^{300}) of −54.0 kcal mol^{-1}, and an entropy (ΔS^{300}) of 81.6 cal mol^{-1} K^{-1}. This leads to a formation constant (K_f^{300}) of 1.8×10^{-20} cm^3 $molecule^{-1}$, at 300 K for reaction 3. At lower temperatures, the formation of the complex is favored. At 200 K, the equilibrium constant increases by over a factor of 200, to 4.8×10^{-18} cm^3 $molecule^{-1}$.

From these data, we can estimate the rate constant for dissociation of the complex, using a method first developed by

Aloisio and Francisco

Troe,[31,32] and further shown to be effective by Patrick and Golden[33] for reactions of atmospheric importance. The dissociation constant (k_{diss}) can be described by the following equation:

$$k_{diss} = Z_{LJ}\rho(E_0)RT(Q_{vib})^{-1}\exp(-E_0R^{-1}T^{-1})F_EF_{anh}F_{rot} \quad (6)$$

where Z_{LJ} is the Lennard-Jones collision frequency; $\rho(E_0)$ is the density of states; R is the gas constant; T is the temperature; Q_{vib} is the vibrational partition function for the associated species; E_0 is the critical energy; and F_E, F_{anh}, and F_{rot} are correction terms for the energy dependence of the density of states, anharmonicity, and rotation, respectively. Using this method, we have estimated k_{diss} at 200 and 300 K to be 1.9×10^{-14} and 4.2×10^{-12} cm^3 molecule^{-1} s^{-1}, respectively.

Using the dissociation constant and the pressure, one can estimate the lifetime of HO_3-H_2O under experimental conditions using the equation:

$$\tau = (k_{diss}[M])^{-1} \quad (7)$$

where τ is the lifetime and $[M]$ is the total number density of molecules. Using the experiment performed by Sridharan et al.[20] as an example, where $[M]$ was on the order of 1×10^{17} molecules cm^3, the lifetime of HO_3-H_2O would be approximately 2 μs at 300 K if water was used. At lower temperatures, this lifetime can be greatly increased. At 200 K, τ is approximately 500 μs due to the slower dissociation constant. This is sufficient time for the HO_3-H_2O complex to

be observed experimentally. This can be compared to the lifetime of HO_3, which can be as short as 50 fs if unstable, or as long as 0.1 μs, if HO_3 is 1 kcal mol^{-1} more stable than OH and O_2.

IV. Conclusion

We have calculated the geometry and energy of a complex between HO_3 and H_2O. These computations show that by forming a complex with water, HO_3 is stabilized by about 6.5 kcal mol^{-1} as calculated at the CCSD(T)/6-311++G(2df,2p)// B3LYP/6-311++G(2df,2p) level of theory. We also show that the lifetime of the HO_3-H_2O complex may be 20 to 500 times longer than that for the HO_3 monomer under reasonable experimental conditions. We feel that water complexation is significant enough to stabilize this otherwise metastable molecule. More importantly, the results suggest the possibility that similar metastable molecules may be stabilized by water complexation.

Although the consequences this has on atmospheric chemistry are unclear, due to the unknown reactivity of HO_3, some speculation can be made. Where water number densities are high, it is likely that H_2O will stabilize HO_3. HO_3 has a sufficient lifetime to react with other molecules. A possible reaction consequence of the HO_3 reaction is the transfer of oxygen from HO_3 to a reactant. Assuming a gas kinetic reaction rate, this reactant would have to have a number density at least on the order of 10^{13} molecule cm^{-3} to compete with dissociation of HO_3.

(31) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4745.
(32) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4758.
(33) Patrick, R.; Golden, D. M. *Int. J. of Chem. Kinet.* **1983**, *15*, 1189−1227.