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Proton Affinity of Methyl Peroxynitrate[†]

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The equilibrium structures, harmonic vibrational frequencies of methyl peroxynitrate, and structures of protonated methyl peroxynitrate have been investigated using ab initio methods. The methods include the single- and double-excitation quadratic configuration (QCISD) methods and the QCISD(T) method, which incorporates a perturbational estimate of the effects of corrected triple excitation. The lowest-energy gas-phase form of protonated methyl peroxynitrate is a complex between CH_3OOH and NO_2^+. The $CH_3OOH\cdot NO_2^+$ complex is bound by 22 ± 2 kcal/mol. The estimated proton affinity of methyl peroxynitrate is 178.8 ± 3 kcal/mol. A general trend for the proton affinity of ROO−NO_2 (peroxynitrates) compounds is discussed.

I. Introduction

In the troposphere, alkyl radicals (R) react with O_2 to form alkylperoxy radicals (RO_2). These radicals primarily react with NO, HO_2, and other RO_2 radicals, but they can also react with NO_3 at night and NO_2[1]

$$R + O_2 + M \rightarrow RO_2 + M \qquad (1)$$

Alkyl peroxynitrates are formed from the reaction of RO_2 with NO_2 and thermally decompose in the reverse of this reaction.[2,3] Its thermal decomposition is an important loss process of peroxynitrates near the earth's surface, where NO_2 undergoes hydrolysis and RO_2 goes on to decompose into other products. The decomposition mechanism of the peroxynitrate species is similar to the decomposition mechanism of $HOONO_2$[4,5]

$$RO_2 + NO_2 + M \rightarrow ROONO_2 + M \qquad (2)$$

$$ROONO_2 + M \rightarrow RO_2 + NO_2 + M \qquad (3)$$

When compared to other competing reactions of RO_2, the formation of alkyl peroxynitrates in the troposphere becomes less significant. These alkyl nitrates are quite unstable with thermal lifetimes on the order of 1 s at room temperature and atmospheric pressure.[2,3] The reaction is relatively fast and occurs under high concentrations of NO_2. Alkyl peroxynitrates can react with NO_2 to form alkyl nitrates ($RONO_2$), belonging to the reactive nitrogen group that accounts for 80% found in the troposphere, and NO_3.[6] They can also rapidly react with NO to form alkyl nitrites (RONO), a storage molecule that contributes to smog formation, and NO_3.[1] The reaction with NO can also form an alkoxy radical (RO) and NO_2, which leads to ozone formation in the troposphere.

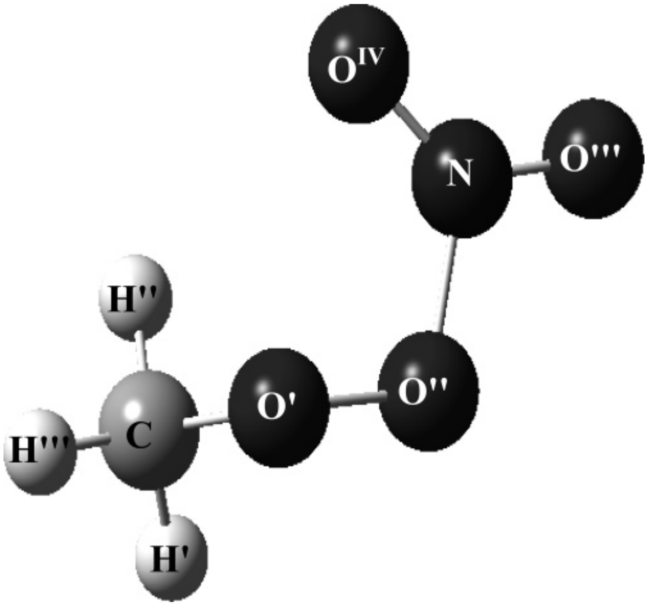

Figure 1. Methyl peroxynitrate (CH_3OONO_2).

Methyl peroxynitrate (CH_3OONO_2) is an important intermediate in the atmospheric oxidation of a variety of organic compounds. It is the simplest member of the alkyl peroxynitrate family. In the stratosphere, its lifetime it is controlled by photodissociation, and in the lower stratosphere, it plays a role in the NO_x budget.[2,3,7] In general, organic peroxynitrates ($ROONO_2$) are large atmospheric reservoirs for peroxy radicals and reactive nitric oxides ($NO_x = NO + NO_2$).[1] Peroxy radicals are important trace tropospheric constituents involved in the oxidation and production of many other atmospheric species central to ozone photochemistry in the troposphere and lower stratosphere. The nitric oxides govern tropospheric ozone formation.

Methyl peroxynitrate has been studied experimentally to determine rate constants for its formation and the rate of thermal decomposition. Sander and Watson[8] used a flash photolysis/

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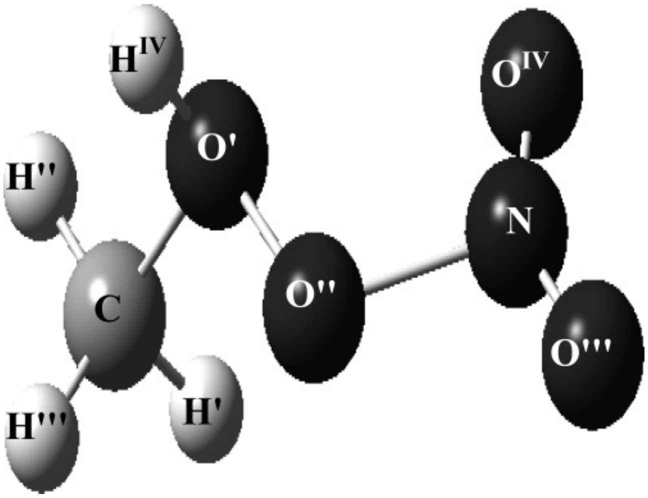

Figure 2. Protonated methyl peroxynitrate (on the first central oxygen).

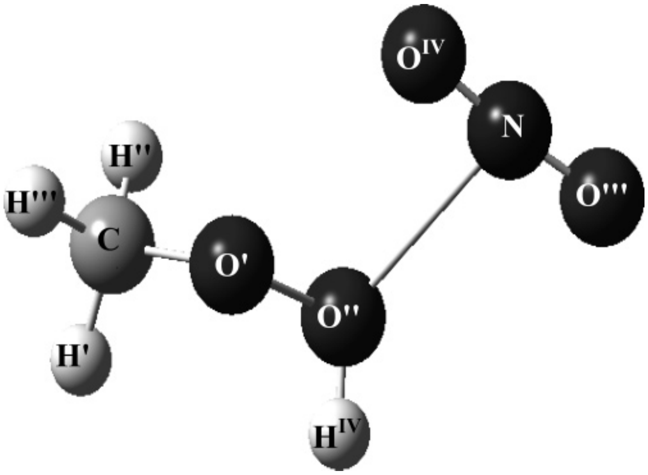

Figure 3. Protonated methyl peroxynitrate (on the second central oxygen; lowest-energy structure).

ultraviolet absorption technique to measure the rate constant for the formation of methyl peroxynitrate at 298K over the pressure range of 50−700 Torr. They found that the formation of methyl peroxynitrate is in the falloff region at 700 Torr and occurs primarily by addition. Bahta et al.[7] and Zabel and co-workers[2,3] have both studied the thermal decomposition kinetics of methyl peroxynitrate. Bahta et al.[7] used ultraviolet absorption at 250 nm to study decomposition over the temperature range of 256−268 K at a total pressure of ∼350 Torr and over the pressure range of 50−720 Torr at 263 K. The data indicate that in the stratosphere, the CH$_3$OONO$_2$ lifetime is determined primarily by photolysis. In the lower stratosphere, the abundance of CH$_3$OONO$_2$ is of the same order of magnitude as the daytime NO$_2$, implying that CH$_3$OONO$_2$ may play a role in the NO$_x$ budget. Zabel and co-workers[2,3] used a temperature-controlled reaction chamber at temperatures between −28 and 0 °C and total pressures from 10 to 800 mbar to study the decomposition of methyl and ethyl peroxynitrate. The concentrations in the experiments are monitored by IR absorption spectroscopy. The data suggested that the lifetime of CH$_3$OONO$_2$ is controlled by photolysis and its decomposition is an important reservoir for both NO$_x$ and CH$_3$OO radicals in the upper troposphere and lower stratosphere.

Surprisingly, little is known about the chemistry of alkyl peroxynitrate species because they are difficult to isolate in the laboratory and to observe directly in the atmosphere.[9] A goal of the present work is to evaluate whether protonation could be a viable method of observing and measuring methyl peroxynitrate. Specific to this assessment is the determination of the proton affinity and byproducts that result from the protonation of methyl peroxynitrate. Knowledge of the proton affinity is needed not only for analytical method development for the detection of methyl peroxynitrate but also is useful for understanding the mechanisms of this species' aqueous phase decomposition.

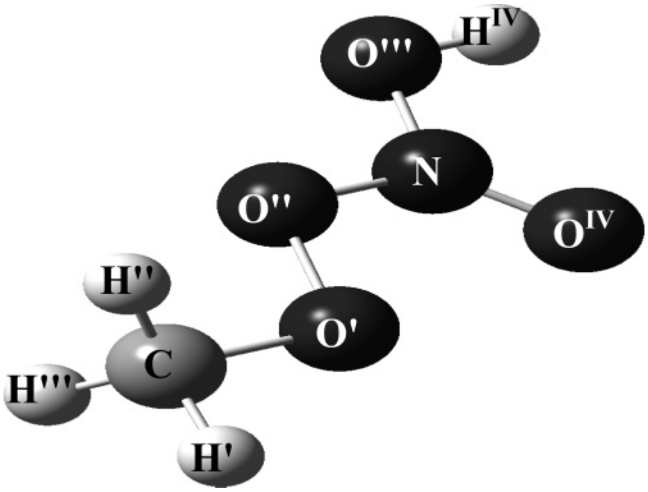

Figure 4. Protonated methyl peroxynitrate (on the tertiary oxygen).

II. Computational Methods

Up until now, ab initio calculations have not been recorded in the literature for this species. We performed our calculations based on methods used for other similar nitrate species to methyl peroxynitrate found in the literature, such as HOONO$_2$.[10] Geometry optimizations for methyl peroxynitrate and of various protonated forms are determined with Becke's three-parameter density functional (B3LYP) method,[11,12] the quadratic configuration interaction with single- and double-excitations (QCISD)[13] method, and the QCISD(T) approach,[13] which incorporates a perturbational estimate of the effects of connected triple excitations. These methods are used with the 6-31G(d) basis set.[14] Harmonic vibrational frequencies are determined for all structures at the B3LYP, QCISD, and QCISD(T) levels of theory, using the 6-31G(d) basis set, to check whether the protonated structures are indeed minimas. Single-point energy calculations are performed with the QCISD(T) method in conjunction with three additional basis sets, 6-311++G(2d,2p), 6-311++G(2df,2p), and 6-311++G(3df,3pd). In addition, the correlation-consistent Dunning basis sets are also used in single-point calculations.[15] The composite methods such as G2(MP2), CBS-Q, and CBS-APNO are also used to predict and determine the energetics and are performed to independently evaluate the QCISD(T) energetics. The composite methods such as G2(MP2) and CBS-Q determine optimized structures at the MP2 level of theory, while the CBS-APNO method determines the optimized structure at the QCISD level of theory. These are quite modest levels of theory for structural determination, which could result in a loss in reliability in the energetics. Nevertheless, these methods have been shown to be reasonable in predicting the proton affinities for PAN-like and nitrate type molecule.[16−18] The Gaussian 03 program[19] is used in all calculations.

III. Results and Discussion

A. Methyl Peroxynitrate (CH$_3$OONO$_2$). Calculated features of the equilibrium structure for methyl peroxynitrate (CH$_3$-

TABLE 1: Proton Affinity[a] for the Protonated Structure of CH_3OONO_2

method	basis set	proton affinity (kcal/mol)			
		CH_3OONO_2	CH_3OOHNO_2	CH_3OHONO_2	CH_3OONO_2H
QCISD(T)	6-31G (d)	0.0	**174.0**	162.9	162.2
	6-311++G (2d, 2p)	0.0	**178.8**	165.0	164.8
	6-311++G (2df, 2p)	0.0	**177.9**	163.9	164.3
	6-311++G (3df,3pd)	0.0	**178.8**	164.6	165.0
	aug-cc-pVDZ	0.0	**176.0**	163.5	162.1
	aug-cc-pVTZ	0.0	**176.8**	164.2	164.3

[a] Values in boldface are for the lowest-energy structure, CH_3OOHNO_2.

TABLE 2: Proton Affinity Values Calculated with the Quadratic Interaction Method for Calibration Set of Molecules

method	basis set	proton affinity	
		NO_2	$HONO_2$
QCISD(T)	6-31G(d)	136.5	178.1
	6-311++G(2d, 2p)	140.6	183.5
	6-311++G(2df, 2p)	139.0	182.1
	6-311++G(3df, 3pd)	140.2	183.1
	experimental	139.6 ± 0.8[a] 140.0 ± 2.0[b]	182.0 ± 2.3[c]

[a] Taatjes, C. A.; Osborn, D. L.; Cool, T. A.; Nakajima, K. *Chem. Phys. Lett.* **2004**, *394*, 19. [b] Polley, C. W.; Munson, B. *Int. J. Mass Spectrom. Ion Processes* **1984**, *59*, 333. [c] Lee, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 8247.

$OONO_2$) are obtained at three levels of theory for the equilibrium structure and are presented in Table 1 of the Supporting Information, and Figure 1 depicts the structure for CH_3OONO_2. There are three dihedral angles that define the conformation of CH_3OONO_2: (1) the HCOO dihedral angle, (2) the COON dihedral angle, and (3) the OONO dihedral angle. The minimum-energy structure for CH_3OONO_2 is a trans, gauche, cis conformation. Table 1 of the Supporting Information shows the close agreement between the B3LYP, QCISD, and QCISD(T) structures. When we compare the QCISD and QCISD(T) structures, the largest change is 0.035 Å in the O−N bond. Between the B3LYP and the QCISD(T) structures, the change in this bond is 0.003 Å.

B. Protonated Methyl Peroxynitrate: A Conformational Study. There are four protonation sites on CH_3OONO_2. There is one protonation site at the nitrogen and three oxygen protonation sites. The dihedral angles that define the oxygen-protonated conformations of CH_3OONO_2 are: (1) the HCOO, (2) the COON, (3) the OONO, and (4) the HOON (first central oxygen), the HONO (second central oxygen), or the ONOH (the last two terminal oxygens) dihedral angles. The substituted oxygen sites are shown in Figures 2−4. Optimization and frequency calculations, using three levels of theory (B3LYP, QCISD, and QCISD(T)), are performed on eight structures of CH_3OONO_2 with two possible conformations (trans or cis) for each protonation site. This resulted in 48 structure evaluations. Table 2 of the Supporting Information shows the structural data for the equilibrium geometries for the lowest-energy structure for the conformers of the protonated CH_3OONO_2 structure. Single-point calculations are performed on all of the protonated structures (Table 1), and further calculations are performed on the lowest-energy structure, using three composite methods: G2-(MP2), CBS-Q, and CBS-APNO (Table 3).

When comparing the QCISD(T) results for the unprotonated O−N bond with those of the O−N bond of the lowest-energy structure, we find a large structural change of 0.87 Å at the QCISD (T) level of theory. The changes in the HCO, COO, OON, and ONO bond angles are between 0.1° and 26.9° after protonation. For the HCOO, COON, and OONO dihedral angles the changes are ∼7°, 39°, and ∼12°, respectively. The lowest-energy structure yields a complex between CH_3OOH and NO_2^+. If we compare this result with the literature results for $HOONO_2$,[10] where the lowest-energy structure yields a complex between HOOH and NO_2^+, then we find that protonation of methyl peroxynitrate also yields an NO_2^+ cation. Total and relative energies for the protonated structures of CH_3OONO_2 are given in Table 3 of the Supporting Information. The main result from the relative energies is to ascertain the lowest-energy isomer of protonated methyl peroxynitrate. Protonation on the second central oxygen site yields the lowest-energy structure. There is an 11.1 kcal/mol difference between the two central protonated oxygen sites and a 0.7 kcal/mol difference between the first central and terminal and an 11.8 kcal/mol difference between the second central and terminal protonated oxygen sites.

C. Proton Affinity of Methyl Peroxynitrate. The proton affinity of CH_3OONO_2 is obtained from the negative of the enthalpy of protonation

$$\mathrm{PA}(CH_3OONO_2) = E_0(H^+) + E_0\,(CH_3OONO_2) - E_0(CH_3OONO_2 - H^+)$$

$E_0(CH_3OONO_2)$ and $E_0(CH_3OONO_2 - H^+)$ are the zero-point-energy-corrected total energies at 0 K for the optimized structures for CH_3OONO_2 and the various protonated structures. Because molecules containing NO bonds are challenging for ab initio methods, proton affinity calculations were performed for NO_2 and $HONO_2$ to calibrate the methods used for evaluating the proton affinity for CH_3OONO_2. Moreover, these molecules were selected because they provide some structural similarity and they have accurate experimental proton affinity measurements against which to calibrate the ab initio results. The results are given in Table 2 and show that the error associated with the calculated proton affinity at the QCISD(T)/6-311++G(3df, 3pd)//QCISD(T)/6-31G(d) level of theory is 1 kcal/mol. This suggests that this level of theory should provide a reasonable estimation of the proton affinity of CH_3OONO_2.

The lowest-energy protonated structure of methyl peroxynirate (CH_3OOHNO_2) is used to determine the proton affinity with composite methods (G2(MP2), CBS-Q, or CBS-APNO) and single-point calculations using the QCISD(T) method with basis sets that range from 6-31G(d) to the enlarged 6-311++G(3df,-3pd) basis set. Table 3 shows the proton affinity for the lowest-energy structure of methyl peroxynitrate, and Table 4 shows the binding energies. At the highest level of theory, QCISD-(T)/6-311++G(3df,3pd)//QCISD(T)/6-31G(d), the proton affinity is estimated to be 178.8 kcal/mol. If we compare this result with the proton affinity of $HOONO_2$ of 175.1 kcal/mol, then there is consistency between the two systems. If we compare methyl peroxynitrate (CH_3OONO_2) with peroxynitric acid ($HOONO_2$), then we find another interesting trend. Both of these species, when protonated on the second oxygen, yield

TABLE 3: Proton Affinity of Methyl Peroxynitrate (0 K)

methods	CH_3OONO_2 (hartree)	$[CH_3OO\ (H^+)]$ (hartree)	proton affinity (kcal/mol)
G2 (MP2)	−394.81122	−395.09358	177.2
CBS-Q	−394.84328	−395.12321	175.6
CBS-APNO	−395.26166	−395.54342	176.8
QCISD/6-31G(d)	−394.27737	−394.56388	173.5
QCISD (T)/6-31G(d)	−394.31732	−394.60461	174.0
QCISD (T)/6-311++G (2d, 2p)	−394.64403	−394.93901	178.8
QCISD (T)/6-311++G (2df, 2p)	−394.76435	−395.05791	177.9
QCISD (T)/6-311++G (3df, 3pd)	−394.79068	−395.08570	178.8
QCISD(T)/aug-cc-pVDZ	−394.49120	−394.78164	176.0
QCISD(T)/aug-cc-pVTZ	−394.82188	−395.11374	176.8

TABLE 4: Binding Energy of the Lowest-Energy Protonated Methyl Peroxynitrate Structure

composite method	total energy[a]		binding energy[b]
	CH_3OOH	NO_2^+	
G2 (MP2)	−190.57707	−204.47987	23.0
CBS-Q	−190.59150	−204.49644	22.1
CBS-APNO	−190.79726	−204.71175	21.6

[a] In units of hartree. [b] In units of kcal/mol.

TABLE 5: Comparison of Proton Affinities for $XONO_2$ and $XOONO_2$ (where X = H and CH_3)

species	proton affinity	reference
$HONO_2$	182.5	22
$HOONO_2$	175.1	10
CH_3ONO_2	176.9 ± 5	22
CH_3OONO_2	178.8	this work

a complex between ROOH and NO_2^+. At the QCISD(T)/6-31G(d) level of theory, we find that the proton affinities are 170.0 kcal/mol[10] for $HOONO_2$ and 174.0 kcal/mol for CH_3OONO_2. We find an increase of ~4 kcal/mol throughout the levels of theory, suggesting a methyl effect as the R group goes from an H group to a CH_3 group. With increasing basis sets 6-311++G(2d,2p), 6-311++G(2df,2p), and 6-311++G(3df,3pd) at the same level of theory (QCISD(T)), we find the same trend. Computing the proton affinities at the various levels of theory for methyl peroxynitrate show that it converges with respect to basis set improvement. We can then compare these results with those found in the literature for peroxynitric acid because the same has been done and shown for peroxynitric acid.[9] Aschi et al.[20] measured the proton affinity for peroxynitric acid from a Fourier transform ion cyclotron resonance (FT-ICR) study. It was found to be 176 ± 3 kcal/mol. So the computed estimate (175.1 kcal/mol at the QCISD(T)/6-311++G(3df,3pd) level) is within the experimental uncertainty. Knowing the proton affinity experimentally and theoretically for peroxynitric acid is important in verifying that the calculations done on methyl peroxynitrate are reliable, because no experimental results exist for this species.

Another interesting comparison is the binding energy in the $NO_2^+ \cdot CH_3OOH$ complex resulting from the protonation of CH_3OONO_2. The binding energy is estimated to be 21.6 kcal/mol at the CBS-APNO level of theory. This seems quite reasonable when compared to the measured binding energy between NO_2^+ and CH_3OH from FT-ICR measurements from the protonation of CH_3ONO_2.[21]

A comparison of proton affinities for $XONO_2$ and $XOONO_2$ species is shown in Table 4. The proton affinities of CH_3ONO_2 (176.9 ± 5 kcal/mol)[22] and $HONO_2$ (182.5 kcal/mol)[23] also show consistency. Methyl nitrate's (CH_3ONO_2) lowest-energy structure is a complex between CH_3OH and NO_2^+ with a proton affinity of 176.9 kcal/mol. Methyl peroxynitrate's (CH_3OONO_2) lowest-energy structure is a complex between CH_3OOH and NO_2^+ with a proton affinity of 178.8 kcal/mol. The proton affinity of $HOONO_2$ is 175.1 kcal/mol, and it too forms a complex between HOOH and NO_2^+. Protonation of methyl nitrite and methyl peroxynitrite both yield NO^+ with a proton affinity in the same range.

Protonation of methyl nitrate and methyl peroxynitrate both yield an NO_2^+ with proton affinities that are quite similar. If we also compare methyl nitrite with methyl nitrate and methyl peroxynitrite with methyl peroxynitrate, then we find that the proton affinities of methyl nitrite and methyl peroxynitrite (188.5 and 188.6 kcal/mol) are larger than those of methyl nitrate and methyl peroxynitrate (176.9 and 178.8 kcal/mol).

If we compare the proton affinities of the $HONO_2$ family, then we also find a trend in terms of their range. Going from $HONO_2$ to $HOONO_2$, we see a decrease in the proton affinity value of 7.4 kcal/mol. In going from CH_3ONO_2 to CH_3OONO_2, we see a slightly larger increase in the proton affinity value of 1.9 kcal/mol. We observe a methyl effect between the $XONO_2$ species (decrease of 5.6 kcal/mol) and the $XOONO_2$ species (increase of 3.7 kcal/mol).

IV. Conclusions

All possible protonated sites and conformations have been examined for methyl peroxynitrate via ab initio, density functional, and composite methods. The present study suggests that there is a distinct protonation pattern for methyl peroxynitrate. We find that the preferred site of protonation is on the second central oxygen, resulting in a complex of CH_3OOH and NO_2^+. Both of these species are detectable using mass spectroscopy. At the QCISD(T)/6-311++G (3df, 3pd)//QCISD(T)/6-31G(d) level of theory, the best estimate of the proton affinity is 178.8 kcal/mol. When comparing the $XONO_2$ and $XOONO_2$ species, we find a general trend between their proton affinities.

Supporting Information Available: Additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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