

## Theoretical Studies for Strong Hydrogen Bonds in Trimethyl Phosphate-(HNO<sub>3</sub>)<sub>n</sub> Complexes, *n* = 1-3

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We have calculated energies and structures for the hydrogen bonded clusters between trimethyl phosphate and nitric acids. The hydrogen bond lengths between phosphoryl oxygen and the proton of nitric acid are short compared to normal hydrogen bonds, and the H-bond strengths are fairly strong. The hydrogen bond length becomes longer, and the strength becomes weaker, as more nitric acids are bound to the TMP. The average H-bond strengths for the TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes with *n* = 1, 2, and 3, are 9.6, 7.9 and 6.4 kcal/mol at 300 K, respectively. Weak hydrogen bonds between nitrate oxygen and methyl proton might contribute to the stability of the clusters. Not only the BSSE but also the fragment relaxation energies should be considered to calculate hydrogen bond strengths for the complexes accurately.

**Key Words** : Strong hydrogen bond, TMP-HNO<sub>3</sub>

### Introduction

The studies of hydrogen-bonded complexes, both experimental and theoretical, are of considerable interest.<sup>1-3</sup> The strength of normal hydrogen bonds is about 1-4 kcal/mol and generally less than 10 kcal/mol. The bond length is about 3 Å between hydrogen donor and acceptor atoms. Recently a special class of hydrogen bonds, so-called low-barrier or short-strong hydrogen bonds, has been proposed as an important factor in enzyme catalysis.<sup>4-10</sup> Notable features of such hydrogen bonds are the short distances between hydrogen donor and acceptor atoms, the strong hydrogen bond energy, the low isotopic fractionation factor, the Hadzi type II IR spectra,<sup>11</sup> and the extreme downfield chemical shift of the proton involved in this type of hydrogen bond.<sup>5,12</sup> Short strong hydrogen bonds are not rare in charged systems in the gas phase. One example is the bifluoride FHF<sup>-</sup> in the gas phase, with the strength of 42 kcal/mol.<sup>13</sup>

Hydrogen-bonded complexes involving organic phosphates play an important role in a variety of chemical processes. Organic phosphates can be used as model systems for understanding biological processes, and also have industrial applications, such as extractants in a number of solvent extraction processes. In particular, tri-*n*-butyl phosphate (TBP) has been known as an extractant for the *uranyl* and *plutonyl* extraction in the PUREX (Plutonium-Uranium-Extraction) process for the reprocessing of spent nuclear fuel and the treatment of nuclear wastes in the nuclear industry.<sup>14-16</sup> In this process, uranium oxides (UO<sub>2</sub>) in the spent fuel are dissolved in strong nitric acid solutions and oxidized to uranyl ions (UO<sub>2</sub><sup>2+</sup>), and the subsequent solvent extractions (in dodecane) with TBP as the active extracting reagent remove uranium as UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub> complexes into the organic phase. Recently, for the green process of nuclear waste treatment, supercritical fluid extraction (SFE) techno-

logy has been utilized for the extraction of some radioactive metal ions.<sup>17,18</sup> Owing to the markedly reduced generation of waste, this new supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) technology has drawn an attention as a green nuclear process. TBP also has been used as an extracting reagent in sc-CO<sub>2</sub> extraction technology because it forms the CO<sub>2</sub>-soluble complex with nitric acid and its complex makes solid uranium dioxides dissolved in sc-CO<sub>2</sub>. Even though the structures of TBP and nitric acid complexes are proposed, and molecular dynamic simulation studies on several model systems of TBP and nitric acid complexes have been reported,<sup>19,20</sup> still the chemical nature of this complex has not been understood clearly.

For better understanding the factor of dissolution of uranium oxides in sc-CO<sub>2</sub>, the molecular level structures of the TBP-HNO<sub>3</sub> complex should be probed. In this paper, we report our theoretical studies on the structure and the hydrogen-bond strength of trimethyl phosphate-(HNO<sub>3</sub>)<sub>n</sub> complexes, *n* = 1-3, to model the TBP-(HNO<sub>3</sub>)<sub>n</sub> complexes.

### Computational Methods

All electronic structure calculations were done using the GAUSSIAN 98 quantum mechanical packages.<sup>21</sup> Geometries for trimethylphosphate (TMP), HNO<sub>3</sub>, and TMP-(HNO<sub>3</sub>)<sub>n</sub>, *n* = 1-3, were optimized initially at the Hartree-Fock (HF) level of theory using the 6-31G(d,p) basis set, and frequencies were calculated at this level and scaled by 0.8929 for the zero-point energies and enthalpies.<sup>22</sup> The final structures for TMP, HNO<sub>3</sub>, and TMP-(HNO<sub>3</sub>)<sub>n</sub>, *n* = 1-3, were optimized at the MP2/6-31G(d,p) level.

The formation energies for the hydrogen-bonded complexes were calculated from the difference in energies between the complex and monomers. These energies correspond to the H-bond strengths. The basis set superposition error (BSSE) may be important in the calculation of the formation ener-

gies.<sup>23</sup> The BSSE was corrected by the Boys and Bernardi counterpoise correction scheme,<sup>24</sup>

$$\text{BSSE} = [E_m(M_1) - E_d(M_1')] + [E_m(M_2) - E_d(M_2')] \quad (1)$$

where M and M' denote the optimized geometry of monomer and the geometry of the monomer in the optimized dimer, respectively, and  $E_m(M)$  and  $E_d(M')$  are the energies of the monomer in its own basis set and in the basis set of the dimer, respectively. The fragment relaxation energy ( $E_{\text{FR}}$ ), *i.e.*, the energy associated with the transition from the optimized geometry of monomer to the geometry that the monomer has in the dimer, should also be considered in addition to the correction of the BSSE.

$$E_{\text{FR}} = [E_m(M_1') - E_m(M_1)] + [E_m(M_2') - E_m(M_2)] \quad (2)$$

One can include the fragment relaxation energy with the BSSE, but we considered them separately. The corrected formation energy is determined as follows:

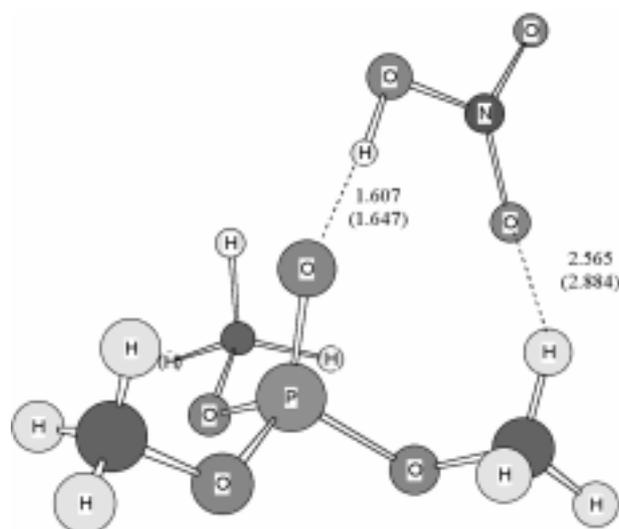
$$E_{\text{HB}}(\text{corr}) = E(D) - [E_m(M_1) + E_m(M_2)] + \text{BSSE} + E_{\text{FR}} \quad (3)$$

where  $E(D)$  is the energy of the hydrogen-bonded dimer.

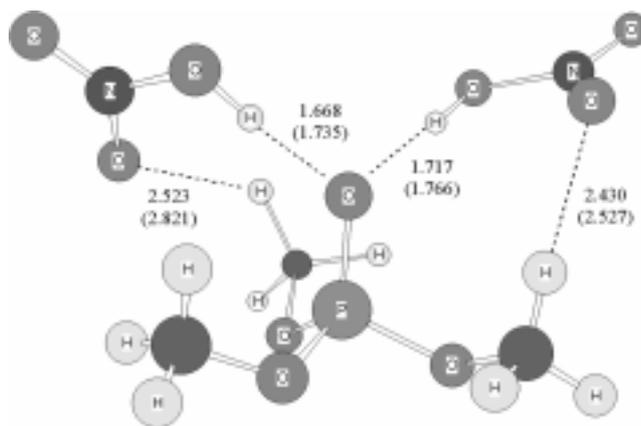
## Results and Discussion

The structures of TMP have recently been calculated at the MP2/6-31G(d) level by S. Singh and coworkers,<sup>25</sup> and they found that there are three possible conformers with  $C_3$ ,  $C_1$ , and  $C_s$  symmetries and the  $C_3$  conformer is the most stable in energy among them. There are two possible hydrogen-bonding sites, one to the *phosphoryl* oxygen and the other to the *alkoxy* oxygen of TMP. Viswanathan and coworkers<sup>26</sup> have reported that the hydrogen bond to the phosphoryl oxygen is about 3 kcal/mol stronger than that to the alkoxy oxygen, when a water molecule is attached. Therefore we have focused on the  $C_3$  conformer with hydrogen bonds to the *phosphoryl* oxygen of TMP.

The HF level of energies and zero-point energies for nitric acids, TMP, and the TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes,  $n = 1-3$ , are listed in Table 1 with the MP2 level of energies using the 6-31G(d,p) basis sets. The optimized structures for TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes,  $n = 1-3$ , are shown in Figures 1-3, respectively. The hydrogen bond length between nitric acid and the *phosphoryl* oxygen of TMP-HNO<sub>3</sub> is 1.607 Å and 1.647 Å at the MP2 and HF levels, respectively, as shown in Figure 1. The HF level of theory slightly overestimates the hydrogen bond length, and this trend has also been reported



**Figure 1.** Structure of TMP-HNO<sub>3</sub> optimized at the MP2 and HF level using 6-31G(d,p) basis sets. Bond lengths are in Å. Numbers in parenthesis are obtained from the HF level.



**Figure 2.** Structure of TMP-(HNO<sub>3</sub>)<sub>2</sub> optimized at the MP2 and HF levels using 6-31G(d,p) basis sets. Bond lengths are in Å. Numbers in parenthesis are obtained from the HF level.

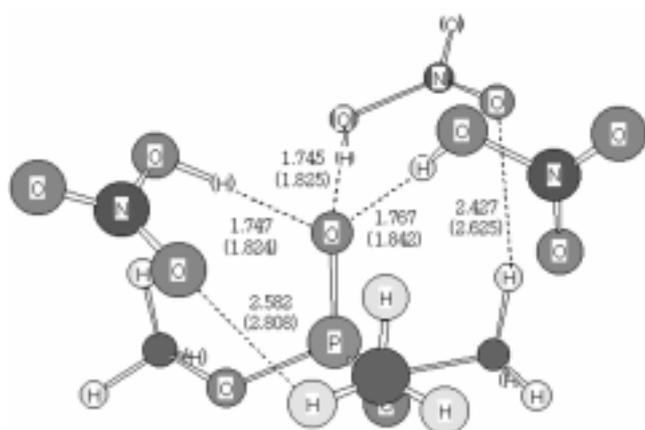
for various hydrogen bonds.<sup>27</sup> This H-bond length is very short compared with those of normal hydrogen bonds between oxygen atoms, *e.g.*, the hydrogen bond between water and formaldehyde, which is about 2 Å.<sup>27</sup> The short distance between the *phosphoryl* oxygen and nitric acid suggests that this hydrogen bond should be quite strong.<sup>28</sup> The distances between nitrate oxygen and methyl proton are 2.565 Å at the MP2 level. This is smaller than the van der Waals distance between these two atoms, 2.6 Å,<sup>29</sup> so one might expect a weak interaction.

There are two H-bonds in TMP-(HNO<sub>3</sub>)<sub>2</sub> as shown in Figure 2. The first H-bond length is 1.668 Å and the second is 1.717 Å at the MP2 level. They are 1.735 and 1.766 Å at the HF level, respectively. Again the HF level slightly overestimates the H-bond length. There are two weak interactions between nitrate oxygen and methyl protons, and their distances are 2.430 Å and 2.523 Å at the MP2 level. Various type of C-H...O hydrogen bonds have been reviewed, and

**Table 1.** Energies and zero-point vibrational energies of nitric acid, trimethyl phosphate, and TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes,  $n = 1-3^a$

	HF/6-31G(d,p)	ZPE <sup>b</sup>	MP2/6-31G(d,p)
HNO <sub>3</sub>	-279.450746	0.026922	-280.176011
TMP	-759.110807	0.128840	-760.375605
TMP-HNO <sub>3</sub>	-1038.585969	0.156814	-1040.577843
TMP-(HNO <sub>3</sub> ) <sub>2</sub>	-1318.052034	0.185161	-1320.773202
TMP-(HNO <sub>3</sub> ) <sub>3</sub>	-1597.513326	0.213430	-1600.967241

<sup>a</sup>Energies are in hartree. <sup>b</sup>Zero-point energies were scaled by 0.8929.



**Figure 3.** Structure of TMP-(HNO<sub>3</sub>)<sub>3</sub> optimized at the MP2 and HF levels using 6-31G(d,p) basis sets. Bond lengths are in Å. Numbers in parenthesis are obtained from the HF level.

generally the interaction with about 2.4 Å of distance can be considered as a weak hydrogen bond.<sup>30</sup>

There are three hydrogen bonds in TMP-(HNO<sub>3</sub>)<sub>3</sub> as shown in Figure 3. The first H-bond length is 1.824 Å and 1.747 Å, the second is 1.825 Å and 1.745 Å, and the third is 1.842 Å and 1.768 Å at the HF and MP2 levels, respectively. These lengths are still quite short compared to normal hydrogen bond lengths between oxygen atoms. The MP2 level predicts two weak interactions again between nitrate oxygen and methyl protons with 2.427 and 2.582 Å of distances. One with 2.427 Å of distance can also be regarded as a weak hydrogen bond, which can contribute to the stability of the complexes.

The formation energies for various H-bonded complexes calculated at the HF and MP2 levels are listed in Table 2. These energies are related with hydrogen bond strengths for the complexes. The formation energies for TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes with  $n = 1, 2,$  and  $3$  are -16.5, -28.6, and -39.9 kcal/mol, respectively, at the MP2 level. The HF level slightly underestimates these formation energies. Individual H-bond strengths for the first, the second, and the third hydrogen bonds to the phosphoryl oxygen of TMP are -16.5, -12.1, and -11.3 kcal/mol, respectively. The HF level slightly underestimates both the total formation energies and the individual H-bond strengths.

The BSSE and fragment relaxation energies may be important in the calculation of the formation energies. Therefore we have calculated the BSSE and fragment relaxation energies,  $E_{FR}$ , and the results are listed in Table 3. It is interesting to note that the BSSEs of the TMP in TMP-(HNO<sub>3</sub>)<sub>2</sub> and TMP-(HNO<sub>3</sub>)<sub>3</sub> at the HF level are negative, which suggest that the structure of TMP have been altered significantly due to the hydrogen bonding. The  $E_{FR}$  values of the TMP in these clusters are much larger than those of nitric acids. In fact, the phosphoryl P=O bond length of the TMP is increased from 1.485 Å to 1.499, 1.513, and 1.527 Å for the TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes with  $n = 1, 2,$  and  $3$ , respectively, at the MP2 level. The BSSEs at the MP2 level are generally larger than those at the HF level, however the  $E_{FR}$  values are

**Table 2.** Formation energies for various hydrogen-bonded complexes calculated at the HF and the MP2 level without the BSSE correction and the fragment relaxation energies<sup>a</sup>

	HF/ 6-31G(d,p)	MP2/ 6-31G(d,p)
TMP + HNO <sub>3</sub> → TMP-HNO <sub>3</sub>	-15.32	-16.46
TMP + 2HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>2</sub>	-24.93	-28.60
TMP + 3HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>3</sub>	-31.55	-39.91
TMP-HNO <sub>3</sub> + HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>2</sub>	-9.61	-12.14
TMP-(HNO <sub>3</sub> ) <sub>2</sub> + HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>3</sub>	-6.62	-11.31

<sup>a</sup>Energies are in kcal/mol.

**Table 3.** The basis set superposition errors and the fragment relaxation energies in hydrogen-bonded TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes,  $n = 1-3$ <sup>a</sup>

	HF/6-31G(d,p)		MP2/6-31G(d,p)	
	BSSE	$E_{FR}$	BSSE	$E_{FR}$
TMP in TMP-HNO <sub>3</sub>	0.28	0.80	1.75	0.82
HNO <sub>3</sub> in TMP-HNO <sub>3</sub>	0.12	1.05	1.78	1.38
TMP in TMP-(HNO <sub>3</sub> ) <sub>2</sub>	-0.49	2.51	2.35	2.38
1st HNO <sub>3</sub> in TMP-(HNO <sub>3</sub> ) <sub>2</sub>	0.30	0.52	1.80	0.61
2nd HNO <sub>3</sub> in TMP-(HNO <sub>3</sub> ) <sub>2</sub>	0.69	0.62	2.34	0.90
TMP in TMP-(HNO <sub>3</sub> ) <sub>3</sub>	-1.99	4.99	2.45	4.65
1st HNO <sub>3</sub> in TMP-(HNO <sub>3</sub> ) <sub>3</sub>	1.06	0.34	3.31	0.54
2nd HNO <sub>3</sub> in TMP-(HNO <sub>3</sub> ) <sub>3</sub>	0.91	0.27	2.47	0.42
3rd HNO <sub>3</sub> in TMP-(HNO <sub>3</sub> ) <sub>3</sub>	0.83	0.30	2.65	0.41

<sup>a</sup>Energies are in kcal/mol.

quite comparable. The fragment relaxation energies of TMP increase with the number of nitric acids that are hydrogen-bonded to its phosphoryl oxygen. It is 0.82 kcal/mol in TMP-HNO<sub>3</sub>, and becomes 2.38 and 4.65 kcal/mol in TMP-(HNO<sub>3</sub>)<sub>2</sub> and TMP-(HNO<sub>3</sub>)<sub>3</sub>, respectively. The  $E_{FR}$  values of nitric acids in TMP-(HNO<sub>3</sub>)<sub>3</sub> are only about one-tenth of that of TMP. This means that the TMP fragment with larger number of hydrogen bonds is reorganized more. On the other hand, the  $E_{FR}$  values of nitric acids become smaller with the number of hydrogen bonds attached to the TMP. This is probably because each nitric acid is less tightly bound to the TMP when more hydrogen bonds are formed. At the MP2 level the BSSE is larger than the  $E_{FR}$  values, except for the TMP of TMP-(HNO<sub>3</sub>)<sub>2</sub> and TMP-(HNO<sub>3</sub>)<sub>3</sub>.

The formation energies and the H-bond strength of each hydrogen bond after correcting the BSSE and the fragment relaxation energy are listed in Table 4. The formation energies of TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes with  $n = 1, 2,$  and  $3$  are -10.7, -18.2, and -23.0 kcal/mol, respectively, at the MP2 level. The enthalpies of formation at 298 K are -9.64, -15.8, and -19.3 kcal/mol, respectively. The H-bond energies for the first, the second, and the third hydrogen bonds are -10.7, -7.50, and -4.78 kcal/mol, respectively. The enthalpies of H-bond formation at 298 K are -9.64, -6.17, and -3.46 kcal/mol, respectively. The strength of each additional H-bond becomes smaller as more nitric acids are attached to the TMP. The average H-bond strengths of TMP-(HNO<sub>3</sub>)<sub>2</sub> and TMP-(HNO<sub>3</sub>)<sub>3</sub> would be one-half and one-third of their

**Table 4.** Formation energies for various hydrogen-bonded complexes calculated at the HF and the MP2 level including the BSSE correction and the fragment relaxation energies<sup>a</sup>

	HF/6-31G(d,p)			MP2/6-31G(d,p)		
	$\Delta E$	$\Delta H$ (0 K)	$\Delta H$ (298 K)	$\Delta E$	$\Delta H$ (0 K)	$\Delta H$ (298 K)
TMP + HNO <sub>3</sub> → TMP-HNO <sub>3</sub>	-13.07	-12.41	-11.99	-10.72	-10.06	-9.64
TMP + 2HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>2</sub>	-20.79	-19.24	-18.39	-18.22	-16.67	-15.82
TMP + 3HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>3</sub>	-24.84	-22.44	-21.12	-23.00	-20.60	-19.28
TMP-HNO <sub>3</sub> + HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>2</sub>	-7.72	-6.83	-6.40	-7.50	-6.60	-6.17
TMP-(HNO <sub>3</sub> ) <sub>2</sub> + HNO <sub>3</sub> → TMP-(HNO <sub>3</sub> ) <sub>3</sub>	-4.05	-3.20	-2.73	-4.78	-3.93	-3.46

<sup>a</sup>Energies are in kcal/mol.

formation enthalpies, so they are 7.9 and 6.4 kcal/mol, respectively. Viswanathan and coworkers<sup>26</sup> have reported that the H-bond strength between the TMP and a water molecule is about 5 kcal/mol at the MP2//HF/6-31G(d,p) level. This is quite similar to the H-bond strength for the third nitric acid. When water molecules and nitric acids coexist in the mixture, the TMP can form hydrogen bond with nitric acids preferentially over the water molecule until the second acid is bound. Further study should be done to see whether the TMP binds with a water molecule or another nitric acid for the third H-bond.<sup>31</sup>

The H-bond lengths of the TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes with  $n = 1, 2,$  and  $3$  are short compared with normal H-bond lengths, and the H-bond strengths are quite strong, therefore it might be possible to measure these H-bonds. Recently NMR spectra of TBP-HNO<sub>3</sub> complexes in CDCl<sub>3</sub> have been measured with various molar ratio of HNO<sub>3</sub> to TBP.<sup>32</sup> When the ratios were 0.95, 1.49, and 2.51, the resonance peaks appeared at 11.5, 11.0, and 10.3 ppm, respectively. These results suggest that strong H-bonds are formed, and the additional nitric acids reduce the H-bond strength. These results are consistent with our theoretical study.

### Conclusions

We have calculated the energies and structures for the hydrogen-bonded clusters between TMP and nitric acids. The hydrogen bond between TMP and nitric acids are fairly strong. Up to three nitric acids can be hydrogen-bonded to the phosphoryl oxygen of the TMP. The average hydrogen bond strengths at 300 K are 9.6, 7.9 and 6.4 kcal/mol for the TMP-(HNO<sub>3</sub>)<sub>n</sub> complexes with  $n = 1, 2,$  and  $3,$  respectively. The strength of each additional H-bond becomes smaller as nitric acids are attached to the TMP consecutively. The H-bond strengths for the first, the second, and the third hydrogen bonds are 9.6, 6.2, and 3.5 kcal/mol, respectively. Weak hydrogen bonds between nitrate oxygen and methyl proton exist and they might contribute to the stability of the clusters. Not only the BSSE but also the fragment relaxation energies should be considered to calculate hydrogen bond strengths for the clusters accurately.

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