



Theoretical study of hydrogen and halogen bond interactions of methylphosphines with hypohalous acids



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ABSTRACT

Ab initio calculations were used to analyze the interactions between hypohalous acids (HOX; X = F, Cl, Br, I) and methylphosphine derivatives (PH_nMe_{3-n}, n = 0–3) at the MP2/6-311++G(2d,2p) level of theory. Interaction of HOX with PH_nMe_{3-n} lead to both hydrogen bond (HOXPH_nMe_{3-n}-HB) as well as halogen bond (HOXPH_nMe_{3-n}-XB) complexes. Stabilities of both HB and XB complexes increase with basicity of the phosphines that is larger for XB complexes. However HB complexes of a phosphine molecule with different HOX are in the same order of stabilities, but XB complexes of heavier hypohalous acids are more stable. Except for HOCl–PH₃, HOCl–PH₂Me and HOCl–PHMe₂ systems, XB complexes have greater stabilities than their HB counterparts in other cases. Electron densities of complexes were characterized with the atoms-in-molecules (AIMs) methodology. The charge transfer within dimers was analyzed by means of natural bond orbitals (NBOs).

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1. Introduction

A halogen bond is an attractive intermolecular or intramolecular interaction of RX...YZ type, where X is a halogen atom (Lewis acid) and YZ is a neutral or anionic molecule (Lewis base) [1,2]. In recent years, the nature of halogen bonds has been explored with many theoretical [3–8] and experimental studies [9–13], such interaction plays a key role in molecular recognition, crystal engineering, and biomolecular systems [14–18]. The importance of halogen bonds within various areas of scientific research is widely recognized, and this mode of interaction has been the subject of several recent reviews and perspectives articles [19–23].

The larger halogen bonded to carbon (and some other elements) often has a region of positive potential on the extension of the covalent bond to halogen atom. The region of positive potential on a halogen's surface is often described as a positive σ -hole [17,24], and has also been termed the electropositive crown [25]. The electrostatic attraction between the σ -hole and the negative Lewis base is the origin of halogen bonds.

The chemical properties of the hypohalous acids, which are powerful oxidizing agents, are of particular interest because they reflect the interplay between the σ -inductive role of the halogen atom in HOX and the repulsive interactions between the lone pairs

of the adjacent oxygen and halogen atoms [26]. A number of studies have characterized the hydrogen bonded cluster formed by hypohalous acids with themselves [27] or with other molecules [28–31]. The HOX species (where X is F, Cl, or Br) are easily produced in atmosphere and they are crucial for most of the ozone removal processes. Thus title complexes in the present study are of great interest in the field of atmospheric chemistry related to ecological aspects as well as in the crystal engineering field.

On the other hand, phosphines are important ligands in coordination chemistry, especially in organometallic compounds [32–35]. They stabilize low oxidation states of metal centers and can be used to modify both the electronic and steric properties of their corresponding derived coordination compounds. Phosphines are difficult to handle, pyrophoric, sensitive to oxidation with air, and extremely malodorous. However, in the last few years, a trend has been seen towards using phosphines in many areas of research. This is undoubtedly due to the new chemistry being developed that hinges on incorporation of phosphines, in asymmetric catalysis, agriculture, along with many important industrial applications. These fascinating compounds are often valuable intermediates for the manufacture of nonflammable materials, lubricant additives, extragents and flotation reagents. In addition, phosphines serve many ubiquitous biomedical uses.

To the best of our knowledge, neither theoretical nor experimental data regarding the structural information of the interaction of phosphines with any of the hypohalous acids is available in the

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literature. In the absence of experimental information, a theoretical analysis of the existence of such complexes and their properties appears to be in order. The present work reports a detailed examination of the stabilities, electronic structure, and vibrational frequencies of these complexes.

2. Computational methods

Calculations were performed using the Gaussian 03 system of codes [36]. The geometries of the isolated HOX and phosphine molecules as well as HOX-phosphine complexes were fully optimized at the MP2 level of theory [37] with the 6-311++G(2d,2p) basis set [38] for all atoms, except iodine, for which the def2-TZVPP [39] (default-2 triple-zeta valence with the large polarization) basis set was used. The contraction scheme of this basis set is [6s5p3d2f] for I atom.

Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of the zero point energy (ZPE). The counterpoise procedure was used to correct the interaction energy for the basis set superposition error [40]. The AIM2000 package [41] was used to obtain bond properties; and to plot molecular graphs. The natural bond orbital (NBO) method [42] has been used to analyze the interaction of occupied and empty orbitals with the NBO program supplied with Gaussian 03.

3. Results and discussion

For association of one molecule of HOX (X = F, Cl, Br, and I) with one molecule of phosphine ($\text{PH}_n\text{Me}_{3-n}$, $n = 0-3$) following types of interactions were proposed: $\text{XO-H} \cdots \text{PH}_n\text{Me}_{3-n}$ (HB), $\text{HO-X} \cdots \text{PH}_n\text{Me}_{3-n}$ (XB), as well as $\text{O} \cdots \text{P}$ interaction between HOX and $\text{PH}_n\text{Me}_{3-n}$. From these starting geometries only hydrogen ($\text{HOXPH}_n\text{Me}_{3-n}\text{-HB}$) and halogen bonded ($\text{HOXPH}_n\text{Me}_{3-n}\text{-XB}$) complexes could be obtained as local minima, Fig. 1.

In the $\text{HOFPH}_3\text{-HB}$, $\text{HOFPH}_2\text{Me-HB}$, $\text{HOFPHMe}_2\text{-HB}$, and $\text{HOF-PMe}_3\text{-HB}$ complexes, hydrogen bond interactions were found between the HOF and phosphine molecules. Our attempts could not optimize $\text{HOFPH}_n\text{Me}_{3-n}\text{-XB}$ adducts. It seems that $\text{F} \cdots \text{P}$ interaction does not have enough strength for leading to these adducts thus starting structures revert to more stable $\text{HOFPH}_n\text{Me}_{3-n}\text{-HB}$ complexes during optimization. This returns to the slightly negative values of the molecular electrostatic potential (MEP) associated with the fluorine atoms in HOF [3,4] that disfavoring its interaction with the lone pair of the phosphorous atom.

Also the $\text{HOCIPH}_3\text{-HB}$, $\text{HOCIPH}_2\text{Me-HB}$, $\text{HOCIPHMe}_2\text{-HB}$, and $\text{HOCIPMe}_3\text{-HB}$ were specified to HB complexes of HOCl with various phosphines. On the other hand, the XB adducts $\text{HOCIPH}_3\text{-XB}$, $\text{HOCIPH}_2\text{Me-XB}$, $\text{HOCIPHMe}_2\text{-XB}$, and $\text{HOCIPMe}_3\text{-XB}$ were also found for the HOCl.

In agreement with previous studies [3] stabilization energies, Table 1 shows HB interactions for PH_3 , PH_2Me and PHMe_2 are stronger than their XB interactions in HOCl-phosphine system. In contrast, for PMe_3 stability of XB complex is greater than HB.

The HB complexes $\text{HOBrPH}_3\text{-HB}$, $\text{HOBrPH}_2\text{Me-HB}$, $\text{HOBrPHMe}_2\text{-HB}$, and $\text{HOBrPMe}_3\text{-HB}$ as well as the XB complexes $\text{HOBrPH}_3\text{-XB}$, $\text{HOBrPH}_2\text{Me-XB}$, $\text{HOBrPHMe}_2\text{-XB}$, and $\text{HOBrPMe}_3\text{-XB}$ were obtained from interaction of HOBr with phosphines.

Stabilization energies of these complexes indicate HB interactions are weaker than XB for HOBr molecule.

Similarly, for HOI-phosphines the HB complexes $\text{HOIPH}_3\text{-HB}$, $\text{HOIPH}_2\text{Me-HB}$, $\text{HOIPHMe}_2\text{-HB}$, and $\text{HOIPMe}_3\text{-HB}$ were obtained as well as the XB complexes $\text{HOIPH}_3\text{-XB}$, $\text{HOIPH}_2\text{Me-XB}$, $\text{HOIPHMe}_2\text{-XB}$, and $\text{HOIPMe}_3\text{-XB}$. According to data in Table 1, the most stable complexes of HOI are associated with XB interactions.

4. Hydrogen bonded complexes of hypohalous acids with phosphine derivatives

Interaction of hypohalous acids with phosphines could lead to corresponding HB type complexes that denoted as $\text{HOXPH}_n\text{Me}_{3-n}\text{-HB}$. In these complexes the HOX molecule behaves as hydrogen bond donor (HBD), and P atom of phosphine acts as hydrogen bond acceptor (HBA) in a $\text{XO-H} \cdots \text{PH}_n\text{Me}_{3-n}$ interaction.

According to our results stability of HB complexes is determined by basicity of phosphine molecules. Basicity of phosphines considering pK_a of their phosphonium ions has the order of $\text{PMe}_3 > \text{PHMe}_2 > \text{PH}_2\text{Me} > \text{PH}_3$. The pK_a 's phosphonium ions are proportional to the base strength of phosphines and given as: -14 , -3.2 , 3.9 and 8.65 for PH_4^+ , MePH_3^+ , Me_2PH_2^+ and Me_3PH^+ , respectively.

Regular increases were found for stabilities of HB complexes with increasing the basicity of phosphine for each HOX molecule. For example stabilization energies of $\text{HOFPH}_n\text{Me}_{3-n}\text{-HB}$ complexes has the order of: -3.26 , -5.05 , -6.38 , and -7.21 , respectively. Also similar trends were seen for other HOX molecules. Plot of variation of SE versus pK_a (acidities of phosphonium ions) show linear relationship between two parameters clearly, Fig. S1.

In contrast, strength of $\text{H} \cdots \text{P}$ interactions of a phosphine molecule does not significantly change by varying hypohalous acid, so that for HB complexes of PH_3 values of SE are in the range of -3.26 to -3.81 , Table 1 and Fig. S2. Similarly, for PH_2Me , PHMe_2 , and PMe_3 the corresponding values are in the ranges of -5.05 to -5.89 , -6.38 to -7.77 , and -7.21 to -8.81 , respectively. These results show that different HOX molecules play similar roles in HB interactions.

Results of intermolecular bond lengths are given in Table 2. The $\text{H} \cdots \text{P}$ distances are in range of 2.250 – 2.418 Å which return to medium to weak hydrogen bond interactions. For HOF the $\text{H} \cdots \text{P}$ distance decreases from 2.418 in $\text{HOFPH}_3\text{-HB}$ to 2.355 , 2.306 , and 2.284 Å in $\text{HOFPH}_2\text{Me-HB}$, $\text{HOFPHMe}_2\text{-HB}$, and $\text{HOF-PMe}_3\text{-HB}$ complexes, respectively. This shortening occurs along with an increase in the stability of related complexes. Similar shortening of $\text{H} \cdots \text{P}$ distances accompanied with increasing stabilities of complexes were found for other HOX molecules. The $\text{H} \cdots \text{P}$ distance becomes shorter going from HOF to HOCl, HOBr, and HOI for each phosphine derivative.

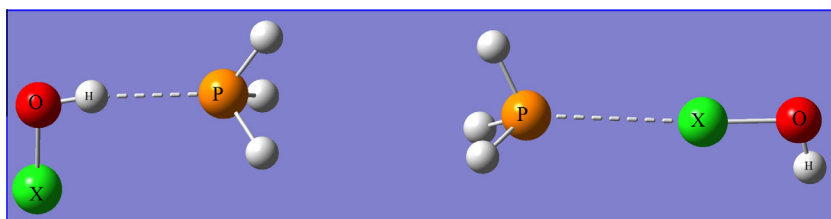


Fig. 1. Schematic representation of HB and XB complexes of phosphines with HOX molecules.

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