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Complexes between hypohalous acids and phosphine derivatives. Pnicogen bond versus halogen bond versus hydrogen bond

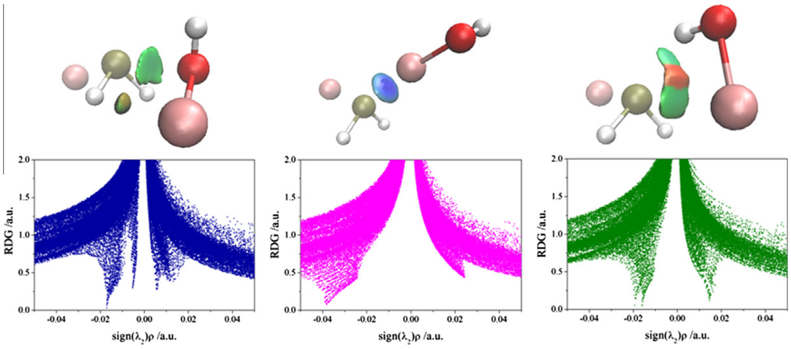
Qingzhong Li, Hongjie Zhu, Hongying Zhuo, Xin Yang, Wenzuo Li, Jianbo Cheng *

The Laboratory of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, People's Republic of China

HIGHLIGHTS

- Three types of complexes were found for the complexes of hypohalous acids and phosphine derivatives.
- There is competition among hydrogen bond, halogen bond, and pnicogen bond.
- This competition is related to the nature of hypohalous acids and phosphine derivatives.

GRAPHICAL ABSTRACT



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ABSTRACT

The complexes of HOBr:PH_2Y (Y = H, F, Cl, Br, CH_3, NH_2, OH, and NO_2), HOCl:PH_2F, and HOI:PH_2F have been investigated with ab initio calculations at the MP2/aug-cc-pVTZ level. Four types of structures (**1**, **2**, **3a**, and **3b**) were observed for these complexes. **1** is stabilized by an O···P pnicogen bond, **2** by a P···X halogen bond, **3a** by a H···P hydrogen bond and a P···X pnicogen bond, and **3b** by H···P and H···Br hydrogen bonds. Their relative stability is related to the halogen X of HOX and the substituent Y of PH_2Y. These structures can compete with interaction energy of $-10.22 \sim -29.40$ kJ/mol. The H—O stretch vibration shows a small red shift in **1**, a small irregular shift in **2**, but a prominent red shift in **3a** and **3b**. The X—O stretch vibration exhibits a smaller red shift in **1**, a larger red shift in **2**, but an insignificant blue shift in **3a** and **3b**. The P—Y stretch vibration displays a red shift in **1** but a blue shift in **2**, **3a**, and **3b**. The formation mechanism, stability, and properties of these structures have been analyzed with molecular electrostatic potentials, orbital interactions, and non-covalent interaction index.

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Introduction

Noncovalent interactions play an extensive and important role in fields of physics, chemistry, and biology [1,2]. With progress of the study on noncovalent interactions, different types of interactions such as hydrogen bond, halogen bond, and pnicogen bond have been proposed [3–5]. Undoubtedly, hydrogen bond is still one of the most important noncovalent interactions, although lots of study has been performed on it. In 2011, a modern evidence-based definition of hydrogen bond was recommended [6]: *The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X—H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.* Halogen bond shares some similarities in structures, properties, strengths, and applications with hydrogen bond, thus in recent years much attention has been paid to it [7–12], due to its potential

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* Corresponding author. Tel./fax: +86 535 6902063.
E-mail address: jbchengyt@sohu.com (J. Cheng).

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applications in molecular recognition [13], crystal materials [14], and biological systems [15]. IUPAC recommendation in 2013 for halogen bond is: *A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity* [16].

Pnicogen bond was recognized as a new and important noncovalent interaction [17–33]. This interaction is analogous to halogen bond since the formation of both interactions is related to the σ-hole on the outer surface of bonded pnicogen and halogen atoms [5]. NBO analyses showed that the lone pair electrons in Lewis bases transfer into the unoccupied orbital of P—X bond directed away from the P atom in pnicogen-bonded complexes involved with PH_2X (X = H, F, Cl, CH_3, NH_2, CF_3, HO, and NO_2) [19]. The electron-withdrawing substituent exerts a strengthening influence on pnicogen bonds [19]; however, the electron-donating substituent NH_2 also brings out a similar enhancing effect, although its influence is smaller. Pnicogen bond was thought to be a new molecular linker in supermolecular chemistry [34] and to be relevant in biological systems [35].

Hypohalous acids as oxidants are involved in the seasonal depletion of the ozone layer in the stratosphere [36–38] and pathophysiological processes [39]. They are a polyfunctional molecule with an acidic proton, an alkaline oxygen, and a halogen with anisotropic electrostatic potentials on its surface, thus hypohalous acids form different types of complexes with themselves [40–42] or other molecules [43–55]. These clusters are helpful for the understanding the role of hypohalous acids in atmospheric chemistry and biological systems.

In the present study, we analyze the complexes of hypobromous acid (HOBr) and phosphine derivatives (PH_2Y, Y = H, F, Cl, Br, CH_3, NH_2, OH, and NO_2) using theoretical calculations. For comparison, the complexes of HOCl:PH_2F and HOI:PH_2F are also studied. Theoretical methods are feasible and necessary for studying these complexes because of chemical instability of hypohalous acids, which makes a difficulty in studying them with experimental methods. Both components have a dual character as a Lewis acid and base, thus it is interesting to know what types of interactions are formed between them, what are the structures of the equilibrium complexes found at these minima, and how do they compare energetically. To characterize these complexes, we analyze the nature of their intermolecular bonds and charge densities.

Computational details

The structures of complexes and their isolated monomers were first optimized at second-order Møller–Plesset perturbation theory (MP2) with the basis set aug-cc-pVDZ for the atoms except iodine, for which the basis set aug-cc-pVDZ-PP was used to take into account for relativistic effects. All structures were then optimized at the MP2/aug-cc-pVTZ(PP) level to obtain more reliable results. Finally harmonic vibrational frequency calculations were carried out at the MP2/aug-cc-pVTZ(PP) level to confirm that the structures obtained correspond to energetic minima. All calculations were performed using the Gaussian09 program [56]. The interaction energy, a difference between the total energy of the complex and the energy sum of the respective monomers, was corrected for the basis set superposition error (BSSE) using the counterpoise method of Boys and Bernardi [57].

Molecular electrostatic potentials (MEPs) on the 0.001 electrons/bohr^3 contour of electronic density were calculated with the Wave Function Analysis–Surface Analysis Suite (WFA–SAS) program [58]. Natural bond orbital (NBO) analyses were obtained with NBO 3.1 version [59] implemented in Gaussian 09 to provide an insight into the bonding nature of these complexes. The atoms in molecules (AIM) analyses were carried out with AIM2000 package [60] to obtain bond topological properties including electron density and Laplacian. The non-covalent interaction (NCI) index was analyzed with the Multiwfn program [61] and its plot was graphed with VMD program [62].

Results and discussion

MEPs of isolated monomers

MEP is a useful tool for identifying basic and acidic centers for intermolecular interactions [63], thus the MEP maps of PH_2F and HOCl as the respective representatives of phosphine derivatives and hypohalous acids are plotted in Fig. 1, and the MEP maps of all monomers are given in Fig. S1. Here we are interested in the MEPs on the P atom of PH_2F. There is a negative MEP region associated with the lone pair on P and a positive MEP region (σ-hole) centered on the extension of the P—Y bond, which is consistent with the previous results [19,28,29]. One can see from Table 1 that when Y of PH_2Y varies from F through Cl to Br, the negative MEP value on the P atom becomes less negative and the positive one at the σ-hole decreases. The negative MEP value on the P atom becomes more negative in the order $OH < H < NH_2 < CH_3$, while the positive MEP at the σ-hole increases in the order $CH_3 < H < NH_2 < OH$. This order is the same as that in Ref. [19]. The MK electrostatic potential charge on the CH_3 group of PH_2CH_3 is 0.059e, indicating the methyl group is electron-donating, which is responsible for the increase of negative MEP value on the P atom and the decrease of positive MEP at the σ-hole in PH_2CH_3 relative to PH_3. This charge is −0.062e and −0.061e for the NH_2 and OH groups, respectively, indicating both groups are electron-withdrawing in PH_2NH_2 and PH_2OH, which is also consistent with the fact that the N and O atoms have greater electronegativity than the P atom. The electron-withdrawing ability of OH group is greater than that of NH_2, which is responsible for the bigger positive σ-hole on the P atom of PH_2OH. The strong electron-withdrawing nitryl group results in a great increase of the positive MEP at the σ-hole and even makes the MEP of the lone pair on P become positive.

For the MEP of HOCl, it is positive on the H atom, negative on the O atom, and anisotropic on the Cl atomic surface, in which a σ-hole is found on the outer surface of bonded Cl atom. This feature was also observed for other hypohalous acids [49–55]. With the increase of X atomic number in HOX, the positive MEP on the H atom decreases, the positive MEP of the σ-hole on the X atom increases, the negative MEP on the X atom decreases, and the negative MEP on the O atom becomes more negative. More negative MEPS are associated with stronger electrophilic sites, while more positive MEPs are indicative of strong nucleophilic sites.

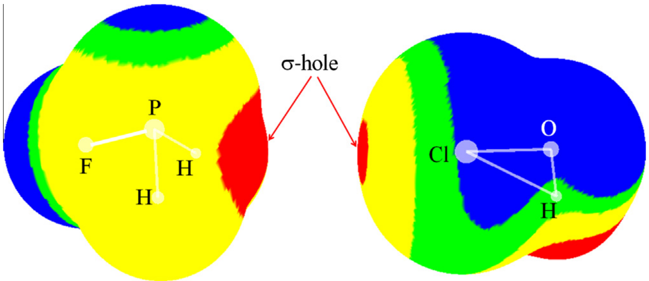

Fig. 1. Molecular electrostatic potentials of PH_2F and HOCl. Color ranges, in eV, are: red, greater than 0.03; yellow, between 0.03 and 0; green, between 0 and −0.01; blue, less than −0.01. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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