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Theoretical investigations of the H···π and X (X=F, Cl, Br, I)···π complexes between hypohalous acids and benzene

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Abstract The H···π and X (X=F, Cl, Br, I)···π interactions between hypohalous acids and benzene are investigated at the MP2/6-311++G(2d,2p) level. Four hydrogen-bonded and three halogen-bonded complexes were obtained. Ab initio calculations indicate that the X···π interaction between HOX and C_6H_6 is mainly electrostatically driven, and there is nearly an equal contribution from both electrostatic and dispersive energies in the case of XOH–C_6H_6 complexes. Natural bond orbital (NBO) analysis reveals that there exists charge transfer from benzene to hypohalous acids. Atom in molecules (AIM) analysis locates bond critical points (BCP) linking the hydrogen or halogen atom and carbon atom in benzene.

Keywords H···π interaction · X···π interaction · Electrostatic potential · σ-hole · Dispersion interaction

Introduction

Non-covalent intermolecular interactions play an important role in molecular recognition, materials science, and biological processes [1–3]. Hydrogen bonds and halogen bonds are the most essential two nonbonded interactions [4–9]. Recently, the reason why halogen-bonded complexes can form has been explained by Politzer et al. [10–19], who recognized that halogen bonding involves the interaction of positive σ-holes—positive regions of electrostatic potential along the direction of the covalent bond to the halogen—with negative sites on other molecules. Fluorine does not participate in halogen bonding because it does not form a positive σ-hole, except when it is linked to some very electrophilic group [11, 12, 20]. It has been observed that the magnitudes of the interaction energies increase with increasing halogen size [9, 10].

Hypohalous acids (HOX, X=F, Cl, Br, I) are involved in stratospheric reactions, the depletion of the ozone layer, and hydroxylation process [21]. Because there are hydrogen and halogen atoms in hypohalous acids, they can be viewed as both hydrogen and halogen bond donors. There have been a great many experimental and theoretical investigations into HOX monomers and the complexes between HOX and other molecules [22–30]. Solimannejad studied the HO_2–HOCl, O_3–HOCl, and HOX–HOX complexes at different computational levels [24–26]. Li et al. [29] carried out ab initio calculations to investigate competition between hydrogen and halogen bonds in complexes of formaldehyde with hypohalous acids. Alkorta et al. [30] located the minima of six structures in complexes between HOX and CO corresponding to two hydrogen bonded complexes, two halogen bonded complexes, and two van der Waals complexes.

Benzene is the most important compound in organic chemistry. Because the π electrons present a negative electrostatic potential, benzene can act as a hydrogen bond or halogen bond acceptor [31–33]. As is well known, benzene has been shown to destroy the atmosphere layer in recent years, and HOX species (X=F, Cl, Br, I) are formed easily in the atmosphere. Our study of the complexes between hypohalous acids and benzene could be of great

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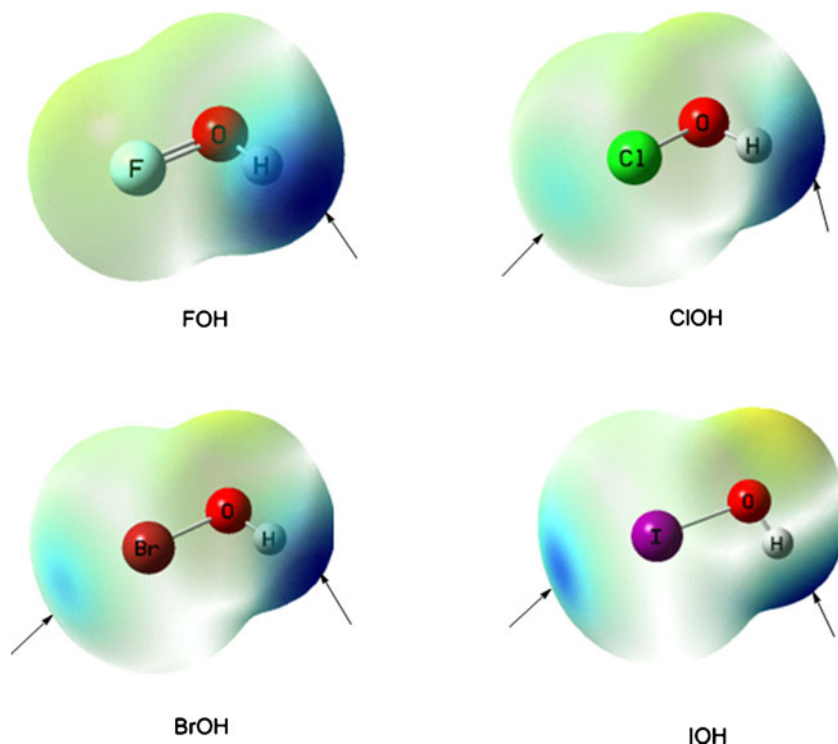Jinan 250100, People's Republic of China

help to the field of atmosphere chemistry relevant to ecological aspects.

In this paper, we systematically studied complexes between HOX (X=F, Cl, Br, I) and benzene using ab initio calculations. Interaction energies and vibrational frequencies were obtained. The orbital and topological properties were investigated with natural bond orbital (NBO) theory and atoms in molecules (AIM) theory. We believe that our theoretical study will enrich the available knowledge of complexes formed in the atmosphere because experimental investigations are rare.

Methods

The structures and energies of monomers and complexes were determined at the MP2/6-311++G(2d,2p) level for all atoms [25–28, 31], except iodine, for which the def2-TZVPP basis set [31, 34] was used. All calculations were carried out using the Gaussian 03 program [35]. The corresponding frequency calculations were carried out at the same level to ensure that the complex structures are true minima. The interaction energies were calculated as the difference between the energy of the complex and the energy sum of the respective monomers. The basis set superposition error (BSSE) was corrected for all calculations by using the counterpoise method proposed by Boys and Bernardi [36].

The bonding characteristics of these complexes were analyzed by using AIM theory [37]. AIM analysis was performed with the software package AIMAll [38] using the MP2/6-311+G(2d,2p) wave functions as input. We also performed NBO analysis [39] by using the MP2/6-311+G (2d,2p) geometries, Hartree-Fock (HF) densities at the same basis set, and the NBO3.1 program in Gaussian 03.

Results and discussion

Electrostatic potential of hypohalous acids HOX

The molecular electrostatic potential of hypohalous acids HOX (X=F, Cl, Br, I) is shown in Fig. 1. There are two maxima in the molecular electrostatic potentials of HOCl, HOBr, and HOI but only one maximum in the molecular electrostatic potential of HOF. The maximal region in the halogen atom was termed the "σ-hole" by Politzer et al. [11]. Table 1 lists the values of the molecular electrostatic potential maximum of HOF, HOCl, HOBr, and HOI. It can be observed that the value of the maximum on the H atom decreases in the following order: HOF>HOCl>HOBr> HOI. This is easy to understand because the electronegativity of the halogen atoms decreases in the same order. For the maximum on the halogen atom, the values increase in the order HOCl<HOBr<HOI. Politzer et al. [10] have summarized an empirical law for the magnitude of the

Fig. 1 Molecular electrostatic potential of the HOX (X=F, Cl, Br, and I) molecule at 0.001 a.u. isosurfaces calculated at the MP2/6-311++G(2d,2p) level. *Blue* denotes maximal molecular electrostatic potential, which is labeled by black arrows; *yellow* denotes negative molecular electrostatic potential. The values of the maximal molecular electrostatic potential are listed in Table 1

Table 1 Maximum of the molecular electrostatic potential (MEP; kcal mol^{-1}) of HOX (X=F, Cl, Br, and I) calculated at the MP2/6-311++G(2d,2p) level

MEP	HOF	HOCl	HOBr	HOI
H side	66.9	61.9	57.3	53.9
X side	-	26.1	34.8	43.8

"σ-hole". For a halogen-containing molecule R-X (X=F, Cl, Br, I), three factors determine the presence or absence and the magnitude of the "σ-hole": (1) the polarizability of the halogen X, (2) its electronegativity, and (3) the electron-withdrawing power of the remainder R of the R-X molecule. It is obvious that the electrostatic potential of HOX fits this law very well. There is no positive "σ-hole" in the F atom of HOF because the OH group is not a strong electron-withdrawing substance. Since polarizability increases and electronegativity decreases from chlorine to iodine, the combined effect is to make the "σ-hole" more positive in the order HOCl<HOBr<HOI.

Interaction energies

The hypohalous acids can act as hydrogen bond or halogen bond donors, and we considered primarily hydrogen-bonded and halogen-bonded complexes. We attempted to find stable structures containing O···π interactions, but failed. All these structures spontaneously reverted to the H···π or X···π complexes. Seven stabilized structures were obtained in our calculations. H···π and X···π complexes have been found between HOX (X=Cl, Br, I) and C_6H_6. For HOF–C_6H_6, only the H···π interaction was detected, which is consistent with the electrostatic potential analysis. Although there have been theoretical reports of fluorine-containing halogen bonded complexes [13, 40], fluorine is not a good halogen bond donor in most halogen bonding interactions.

Table 2 reports the interaction energy results for the HOX (X=F. Cl, Br, I)–C_6H_6 complex; all the interaction energies at the MP2/6-311++G(2d,2p) level are much smaller than those of the O(N)···H and O(N)···X interaction, but have the same order as the CH···π and π···π complexes. The interaction energies (ΔE) are −3.50, −3.93, −3.97, and −4.22 kcal mol^{-1}, respectively, for the C_6H_6–HOF, C_6H_6–HOCl, C_6H_6–HOBr, and C_6H_6–HOI complexes. The H···π interactions become stronger as the polarizabilities of the halogens increase and their electronegativities decrease. This result seems to contradict the electrostatic potential of HOX, as the value of the maximum of the electrostatic potential on the H atom of HOX decreases in the order HOF>HOCl>HOBr>HOI. There are other reasons for this nonconformity; for example, Kim et al. [41] found that the

H···π interaction between HCl and C_6H_6 was larger than that between HF and C_6H_6. Alkorta and co-workers [30] concluded that the ClOH–OC (ClOH–CO) complex was more stabilized than the FOH–OC (FOH–CO) complex. Considering that the electron donor in our calculation is benzene, this consequence is not surprising. In complexes containing an X···π interaction, simple electrostatic models may come under fire [42]. For example, in the CH···π interaction, the major source of attraction is the dispersion interaction and the electrostatic contribution is small, whereas the electrostatic interaction is mainly responsible for attraction in conventional hydrogen bonds [33, 43, 44]. To estimate the magnitude of the dispersion interaction in the H···π complexes between HOX and C_6H_6, we calculated the dispersion interaction energy of the four complexes at the PBE/TZ2P level using the ADF program [45], as shown in Table 2; the absolute value of ΔE_{dis} increases in the following order: FOH–C_6H_6<ClOH–C_6H_6<BrOH–C_6H_6< IOH–C_6H_6, which is accordance with our hypothesis.

Considering the complexes containing an X···π (X=Cl, Br, I) interaction, the nature of the halogen atom plays a prominent role in the strength of the X···π contact. It has been observed that a halogen's σ-hole becomes larger and more positive as the size of the halogen atom increases, with a corresponding tendency for the halogen bond to become stronger [9, 10]. Table 2 shows that the interaction energy at the MP2/6-311++G(2d,2p) level become more negative (stabilizing) as the size of halogen atom increases [10], which is consistent with the electrostatic potential of HOX. The value of the maximum of the electrostatic potential on the halogen atom of HOX increases in the order HOCl<HOBr<HOI. To sum up, the X···π interaction between HOX and C_6H_6 is mainly electrostatically driven, and there is an almost equal contribution from both

Table 2 Basis set superposition error (BSSE)-corrected interaction energies (ΔE, kcal mol^{-1}) at the MP2/6-311++G(2d,2p) level and dispersion interaction energies (ΔE_{dis}, kcal mol^{-1}) at the PBE/TZ2P level[a]

Complex	ΔE	ΔE_{dis}
FOH-C_6H_6	-3.50	-2.59
ClOH-C_6H_6	-3.93	-2.98
HOCl-C_6H_6	-2.04	-1.75
BrOH-C_6H_6	-3.97	-3.26
HOBr-C_6H_6	-3.35	-2.26
IOH-C_6H_6	-4.22	-3.79
HOI-C_6H_6	-4.73	-2.92

[a] ΔE was calculated using the program Gaussian 03. For iodine, the def2-TZVPP basis set was used. ΔE_{dis} was calculated using the ADF program. All these energies were calculated using optimized structures at the MP2 level

Table 3 Calculated natural bond orbital (NBO) parameters of complexes at their equilibrium geometries: second-order orbital interaction energies (in kcal mol^{-1}) and charge transfer (CT, in me)

complex	$E(2)$	CT
FOH–C$_6$H$_6$	2.56	2.89
ClOH–C$_6$H$_6$	2.58	2.02
HOCl–C$_6$H$_6$	3.88	6.12
BrOH–C$_6$H$_6$	1.99	2.01
HOBr–C$_6$H$_6$	4.75	10.63
IOH–C$_6$H$_6$	2.04	0.72
HOI–C$_6$H$_6$	8.76	20.76

electrostatic and dispersive energies in the case of the XOH-C$_6$H$_6$ complex.

From Table 2 one can also see that the H···π complexes are more stabilized than the X (X=Cl, Br)···π complexes. For HOI and C$_6$H$_6$, the strength of the HOI···π interaction is a little stronger than the IOH···π interaction (−4.73 vs −4.22 kcal mol^{-1}). Our calculation confirms that there is a competition between hydrogen bonding and halogen bonding, which has been verified by experimental and theoretical researches [29, 30, 45–47].

NBO analysis

NBO analysis was carried out at the MP2/6-311++G(2d,2p) level using the HF density to reveal the orbital interaction in the HOX–C$_6$H$_6$ complexes. In the hydrogen-bonded and halogen-bonded complexes in which O and N atoms are electron donors, an orbital interaction occurs between the lone pairs of O and N and the antibonding R–H (X) orbitals. If the electron donor is benzene, the contributive orbital becomes the π electron orbital. Table 3 lists the second-order orbital interaction energies $E(2)$ based on the $\pi \rightarrow \sigma^*$ (O–H) and $\pi \rightarrow \sigma^*$ (O–X) orbital interactions in the HOX–C$_6$H$_6$ complexes. One can see from Table 3 that the values of $E(2)$ in the X···π complexes are significantly larger than those of the H···π complexes, which is consistent with that of the interaction energies. For the X···π interaction, $E(2)$ presents a consistent order with the interaction energy, but in the H···π complexes, these two parameters do not show any correlation. This result indicates that the H···π interaction is more complicated than the X···π interaction between HOX and C$_6$H$_6$.

A charge transfer (CT) occurs from the electron donor to the electron acceptor upon formation of hydrogen and halogen bonds. Table 3 also lists the amount of CT in the HOX-C$_6$H$_6$ complexes. As we can see, in all cases, there is a small but non-negligible amount of charge transfer, ranging between 0.72 and 20.76 me from C$_6$H$_6$ to HOX. One can see from Table 3 that the charge transfer in the H···π complexes is very small (from 0.72 to 2.89 me); in the HOI-C$_6$H$_6$, HOCl-C$_6$H$_6$, and HOBr-C$_6$H$_6$ complexes, this value is 6.12, 10.63, and 20.76 me respectively. As the size of the halogen atom increases, the charge transfer decreases in the hydrogen-bonded complexes, whereas it increases in the halogen-bonded complexes. It is noteworthy that the variation of CT is consistent with that of electrostatic potential of HOX, but only partly accordant with the interaction energy. For the H···π complexes, the charge transfer is not consistent with the interaction energy, which is in accordance with the above discussion about the significant role of dispersion interaction in these complexes. The order of the CT is the same as that of the interaction energy in the X···π complexes, indicating the electrostatically driven nature of such nonbonded interactions.

AIM analysis

AIM theory is based on a topological analysis of the electron charge density and its Laplacian, and has been applied successfully to characterize hydrogen bonds and halogen bonds of different strengths in a wide variety of molecular complexes [48–50]. With this in mind, we performed a topological analysis to gain more insight into the nature of the HOX–C$_6$H$_6$ complexes. Our result shows that a bond path exists linking the hydrogen or halogen atom with one carbon atom of benzene accompanied by a bond critical point (BCP). The results of AIM analysis are summarized in Table 4. Because AIM analysis does not support pseudo potential, we did not analyze the complexes between HOI and C$_6$H$_6$. The electron densities ρ_b and their Laplacians are given. The local one-electron kinetic energy densities G_b and local potential energy densities V_b at BCPs, are also included.

The BCPs have a small values of electron density (from 0.0119 to 0.0165) and positive Laplacian, indicating the

Table 4 Bond critical point (BCP) properties (in a.u.) for the HOX (X=F, Cl, Br)–C$_6$H$_6$ complexes

Complex	ρ_b	Lapalcian	ε	V_b	G_b	H_b
FOH-C$_6$H$_6$	0.0135	0.0424	2.1585	-0.0082	0.0094	0.0012
ClOH-C$_6$H$_6$	0.0145	0.0439	1.2645	-0.0090	0.0099	0.0009
HOCl-C$_6$H$_6$	0.0119	0.0411	3.7093	-0.0068	0.0085	0.0017
BrOH-C$_6$H$_6$	0.0141	0.0428	1.2128	-0.0086	0.0097	0.0011
HOBr-C$_6$H$_6$	0.0165	0.0361	2.4807	-0.0065	0.0078	0.0013

typical closed-shell type of interaction in these complexes. Table 4 also gives the ellipticity ε in the HOX–C_6H_6 complexes. Diagonalization of the Hessian of the electron density yields three eigenvalues (λ_1, λ_2, and λ_3). The ellipticity, ε, which is defined as $\lambda_1/\lambda_2 - 1$, provides a measure of not only the π character of a bond but also the bond stability. The ellipticity order is consistent with that of the interaction energy, as shown in the above section.

The electronic energy density of the charge distribution H_b, and the sign of the H_b may be determined by the sum $H_b = G_b + V_b$. Lu et al. [32] have found that weak nonbonded interactions exhibit positive values for both Laplacian and H_b, and, for strong nonbonded contacts, Laplacian is positive and H_b is negative. It is evident from Table 4 that all the values of H_b in the complexes between hypohalous acids and benzene are positive, which shows that the H⋯π and X⋯π interactions between HOX and C_6H_6 are all weak nonbonded interactions.

Conclusions

The H⋯π and X (X=F, Cl, Br, I)⋯π interactions between hypohalous acids and benzene were investigated at the MP2/6-311++G(2d,2p) level. Four hydrogen-bonded and three halogen-bonded complexes were obtained. The X⋯π interaction between HOX and C_6H_6 is mainly electrostatically driven, and there is an almost equal contribution from both electrostatic and dispersive energies in the case of XOH–C_6H_6 complexes. The charge transfer interaction also plays an important role in the nonbonded interactions, as suggested by NBO analysis. BCPs linking the hydrogen or halogen atom and carbon atom in benzene were determined by performing a topological analysis in the context of the AIM theory.

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