



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

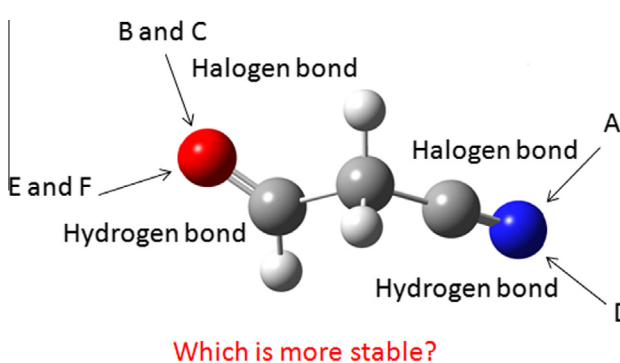
A quantum chemical study of the structures, stability, and spectroscopy of halogen- and hydrogen-bonded complexes between cyanoacetaldehyde and hypochlorous acids

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HIGHLIGHTS

- Six structures are formed between cyanoacetaldehyde and hypochlorous acid.
- The hydrogen-bonded complexes are more stable than the halogen-bonded complexes.
- The associated O–H and O–X stretch vibrations show a red shift.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 September 2013

Accepted 15 October 2013

Available online 30 October 2013

Keywords:

Cyanoacetaldehyde
Hypochlorous acids
Halogen bond
Hydrogen bond
Competition

ABSTRACT

The complexes of cyanoacetaldehyde and hypochlorous acid (HOX, X = Cl, Br, and I) have been investigated. They can form six different structures (A, B, C, D, E, and F), the former three structures are mainly combined through a N(O)···X halogen bond and the latter three structures are maintained mainly by a N(O)···H hydrogen bond, although other weaker interactions are also present in most structures. The hydrogen-bonded structures are more stable than the respective halogen-bonded structures. The O–H and O–X bonds in the halogen- and hydrogen-bonded complexes are lengthened and show an observed red shift, while those in the weaker secondary interactions are contracted and display a small blue shift. The orbital interactions in NBO analysis and the electron densities in AIM analysis provide useful and reliable information for the strength of each type of interaction in different structures.

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Introduction

Cyanoacetaldehyde (N≡CCH₂CHO, CA), a potential prebiotic compound, has aroused people's interest because it can form in a spark discharge reaction in a methane–nitrogen mixture [1] and has been found in the interstellar medium [2], in comets [3], and in Titan's atmosphere [4]. CA has been proposed as a precursor for the prebiotic formation of the pyrimidine bases cytosine and

uracil [5]. Addition of water to cyanoacetylene, a prominent interstellar compound, could produce CA [6], although the activation energy is relatively high even for the protonated cyanoacetylene [7]. Rotational spectrum showed that CA is strongly preferred over its tautomer cyanovinylalcohol (NCCH=CHOH) in the gas phase and the conformer having a non-planar structure with a O–C–C–C dihedral angle of about 150° is more stable than the other conformer with a planar structure, which corresponds to the synperiplanar form of the cyano and carbonyl groups [8]. The dynamical instability of CA results in the fact that it usually exists as a mixture of rotameric forms in the gas phase. This makes a difficulty to

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synthesize CA under laboratory conditions. The first preparative synthesis and isolation of CA were performed in the flash vacuum pyrolysis of isoxazole with a low-temperature partial condensation of the gaseous flow some years ago [9]. Very recently, gas-phase infrared spectra of CA were reported and their assignment was presented with the help of density functional theory and high-level ab initio calculations [10].

Hypohalous acids are important in the field of atmospheric chemistry because HOCl and HOBr are involved in catalytic cycles in the seasonal depletion of the ozone layer in the stratosphere [11,12]. In addition, they, as oxidants with potent antibacterial properties [13], are closely associated with protein science [14] and diseases [15]. It is essential to determine quantitatively and selectively the secretion of endogenous HOCl [16], due to the pathophysiological importance of HOCl. However, the chemical instability of hypohalous acids causes it difficult to experimentally study their properties. Theoretical studies have shown that hypohalous acids can form clusters with themselves [17,18], some nitrogenated bases [19–21], and some oxygenated bases [22–24]. These clusters are stabilized through hydrogen or halogen bonds. In general, the hydrogen-bonded clusters are more stable than the halogen-bonded ones. Both types of interactions play important roles in many fields including molecular recognition and materials science [25,26].

The title complexes in the present work are of interest in the fields of atmospheric chemistry and biology, thus we presented a detailed examination of the electronic structures, stabilities, and vibrational frequencies of these complexes by means of quantum chemical calculations. The chemical instability of hypohalous acids as well as coexistence of CA and its isomers make theoretical calculations to be an efficacious method for studying the title complexes. Both cyano and carbonyl groups in CA can accept the proton and halogen atom from the hypohalous acids, thus the title complexes can be used to study the competition between hydrogen bonds and halogen bonds.

Theoretical methods

All calculations were performed using the Gaussian 09 package of codes [27]. The geometries of complexes and monomers were optimized by using the second-order Møller–Plesset perturbation theory (MP2) with the aug-cc-pVTZ basis set for all atoms, except the iodine, for which the aug-cc-pVTZ-PP basis set was used. This level of theory has been demonstrated to be reasonable for studying hydrogen-bonded complexes [28–30] and halogen-bonded complexes [31–33]. Harmonic vibrational frequency calculations at the same level of theory were used to identify the local minima structures on the potential energy surfaces. The interaction energy was calculated as the difference between the complex energy and the sum of the monomer energy. The counterpoise procedure suggested by Boys and Bernardi [34] was used to correct the interaction energy for the basis set superposition error (BSSE). The AIM2000 program [35] has been used to obtain electron densities and Laplacians at the bond critical points (BCPs) and to plot molecular graphs. The natural bond orbital (NBO) method [36] was used to analyze the interaction of occupied and empty orbitals via the NBO program supplied with Gaussian 09. Molecular electrostatic potentials (MEPs) of CA and HOX have been obtained using the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) program [37].

Results and discussion

MEPs of monomers

It has been evidenced that CA has two stable isomers and one with the C(N)–C–C–O dihedral angle of about 150° is more stable

than the other with the dihedral angle of 0° [8]. In addition, CA also has three tautomers (cyanovinylalcohol), although they are less stable than CA [10]. Thus we considered only the most-stable isomer of CA in the present work. At the MP2/aug-cc-pVTZ level, the C(N)–C–C–O dihedral angle is calculated to be about 145°, which is close to the value reported in the reference. The cyano and carbonyl groups exist in CA simultaneously and both of them act as Lewis bases, as shown by the negative electrostatic potentials (blue regions) on the N and O atomic surfaces in Fig. 1. As expected, the N end shows a more negative electrostatic potential than the O end.

One can see from Fig. 1 that the H atom in HOX (X = Cl, Br, and I) shows positive electrostatic potentials (red area) and its most positive electrostatic potential becomes smaller for the heavier halogen atom. This is consistent with the electronegativity of halogen atom. The halogen atom with greater electronegativity and stronger electron-withdrawing ability leads to a greater acidic proton in HOX. A region of positive electrostatic potential (σ -hole) is also found on the outer side of the halogen atom and its most positive electrostatic potential becomes larger with the increase of X atomic mass. The lone-pair electron on the halogen atom shows a negative electrostatic potential and its value reduces gradually from Cl to I. However, the negative electrostatic potential on the O atom increases in the same order.

Geometries and frequency shifts in the complexes

On the base of electrostatic potentials of CA and HOX, six structures (A, B, C, D, E, and F) are obtained for each HOX. The optimized structures are shown in Fig. 2. In structure A, the halogen atom in HOX approaches the N atom in CA by a halogen bond, and the O–X–N angle is close to 180°. However, for structures B and C, the halogen atom in HOX approaches the O atom in CA. The distance between the methylene hydrogen atom in CA and the X atom in HOX is 2.908 Å in CA–HOCl–B, 2.874 Å in CA–HOBr–B, and 2.980 Å in CA–HOI–B. They are shorter than the sum of the van der Waals Radii of the respective atoms. However, the distance between the formyl hydrogen in CA and the X atom in HOX is greater than the sum of the van der Waals Radii of the respective atoms. Thus, a H···X contact is also present in structure B, besides a O···X halogen bond, while only the O···X halogen bond exists in

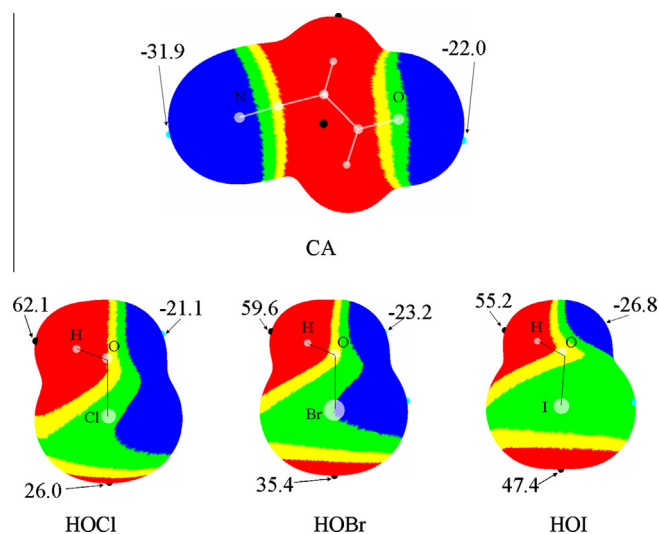


Fig. 1. MEP maps of CA and HOX (X = Cl, Br, and I). Color ranges, in kcal/mol, are: red, greater than 6.3; yellow, between 6.3 and 0; green, between 0 and –6.3; blue, less than –6.3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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