

# Theoretical investigation of the interaction between monohalogenated ethenes and hydrogen peroxide

Pham Ngoc Diep<sup>a</sup>, Hue Minh Thi Nguyen<sup>a</sup>, Tran Thanh Hue<sup>a</sup>, Thérèse Zeegers-Huyskens<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry and Center for Computational Science, Hanoi National University of Education, Viet Nam

<sup>b</sup> Department of Chemistry, University of Leuven, 3001 Heverlee, Belgium

## ARTICLE INFO

### Article history:

Received 16 November 2009

Received in revised form 26 January 2010

Accepted 26 January 2010

Available online 1 February 2010

Dedicated to Professor Austin Barnes

### Keywords:

Monohalogenated ethers–hydrogen peroxide complexes

Ab initio calculations

Blue shifts of the CH stretching vibrations

## ABSTRACT

The complexes between monohalogenated ethenes  $\text{CH}_2=\text{CHX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) and hydrogen peroxide (HP) have been studied theoretically at the MP2/6-311++G(3df,2p) level. The calculations include the optimization of the geometries, the vibrational frequencies and IR intensities of the  $\nu(\text{OH})$  and  $\nu(\text{CH})$  vibrations along with a natural bond orbital (NBO) analysis. The most stable complexes having binding energies between 7 and 12  $\text{kJ mol}^{-1}$  have a cyclic structure characterized by  $\text{OH}\cdots\text{X}$  and  $\text{CH}\cdots\text{O}$  hydrogen bonds. Less stable complexes having binding energies of 6  $\text{kJ mol}^{-1}$  are stabilized by two  $\text{CH}\cdots\text{O}$  hydrogen bonds. The complexes are slightly more stable than the corresponding  $\text{CH}_2=\text{CHX} \cdot \text{H}_2\text{O}$  complexes, showing the predominance of the proton donor in determining the hydrogen bond energies. The variations of the NBO charges on the two partners are discussed. Blue shifts are predicted for the  $\nu(\text{CH})$  vibrations of the  $\text{CH}\cdots\text{O}$  bonds and red shifts for the  $\nu(\text{OH})$  vibrations in the  $\text{OH}\cdots\text{X}$  bonds. The data are discussed as a function of the change in hybridization of the C atom along with the occupation of the  $\sigma^*(\text{CH})$  orbitals. Intramolecular and intermolecular hyperconjugations are discussed as well. The geometric data and NBO parameters suggest that the strength of the  $\text{CH}\cdots\text{O}$  hydrogen bonds are ordered according to  $\text{CH}_2=\text{CHF} < \text{CH}_2=\text{CHCl} < \text{CH}_2=\text{CHBr}$ . An inverse order is found for the  $\text{OH}\cdots\text{X}$  hydrogen bonds.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

The usefulness of hydrogen peroxide (HP) in many fields such as atmospheric chemistry [1], photodissociation dynamics [2], and oxidation reactions [3] is well known. HP is also a byproduct of several metabolic reactions [4] and recent findings suggest that any biological effects of HP in aqueous solution are actually mediated by hydrogen bonding with other compounds [5]. It is therefore of prime importance to investigate the interaction between HP and organic or bioorganic molecules. Although numerous studies have been carried out on the water complexes, relatively few studies were conducted on the interaction with organic molecules. It must be mentioned that theoretical calculations have been carried out on the interaction between HP with water [6,7], hydrogen halides [8], urea [9] and the nucleobases adenine [10], uracil [11] and cytosine [12]. Recently, the interaction between HP and methylhalides [13,14], formamide [15], the hydroperoxyl OOH radical [16] and 2-methylol oxirane [17] has been investigated as well.

In the present work, the interaction between monohalogenated ethenes ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) and HP is investigated by the MP2 method using the extended 6-311++G(3df,2p) basis set. We want to

compare the theoretical results with those recently reported for the complexes between the same ethene derivatives and water [18]. Our study includes the optimization of the geometries, the calculation of the binding energies and relevant vibrational frequencies along with a natural bond orbital analysis including the charges on the different atoms, the occupation of selected antibonding orbitals and the hyperconjugation energies. A special attention will be given to the changes of the parameters connected with the  $\text{CH}(\text{X})$  bonds of the ethene derivatives. To the best of our knowledge, no experimental data have been reported for these systems.

## 2. Computational methods

Ab initio calculations were performed using the GAUSSIAN-03 package of programs [19]. The calculations were carried out at the MP2/6-311++G(3df,2p) level using the MP2/6-31++G(d,p) optimized geometries. The interaction energies were obtained as the difference between the energies of the complexes and the respective monomers, and corrected for basis set superposition errors (BSSEs) using the counterpoise method [20]. Harmonic vibrational frequencies calculated at the same level were retained unscaled since the main goal of our study is to discuss the changes resulting from the interaction between the molecules. Charges on individual

\* Corresponding author.

E-mail address: [therese.zeegers@chem.kuleuven.be](mailto:therese.zeegers@chem.kuleuven.be) (T. Zeegers-Huyskens).

atoms, populations of molecular orbitals, coefficients of the hybrid orbitals and hyperconjugation energies were obtained by the natural bond orbital (NBO) population scheme [21], using the B3LYP functional [22] and the MP2 optimized geometries.

### 3. Results and discussion

#### 3.1. Optimized structures and interaction energies

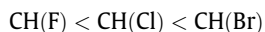
For the 1–1 adducts of  $\text{CH}_2=\text{CHX}$  and  $\text{H}_2\text{O}_2$ , several stable structures were found on the potential energy surface. These structures illustrated in Fig. 1 are cyclic. All the intermolecular distances are shorter than the sum of the van der Waals radii and the intermolecular angles larger than  $90^\circ$ . In the A and B structures, one of the OH bond of HP is acting as a proton donor and the O atom of the other O atom as a proton acceptor, leading to the formation of a seven- (A) or six- (B) membered structure. In the AK and BK structures, the same OH group of HP is acting as a proton donor and proton acceptor. In the anti-cooperative C structure, the two O atoms of HP are acting as proton acceptor. In the monomers as well as in the complexes, the  $\text{CH}_2=\text{CHX}$  molecules are planar or nearly so, the dihedral  $\text{C4C1H5X3}$  angles being comprised between  $179.2^\circ$  and  $180^\circ$ .

The interaction energies including ZPE- and BSSE-corrections are reported in Table 1. For the complexes between the three ethene derivatives and HP, the energies are ordered as

$$\text{A, B} > \text{AK, BK} > \text{C}$$

The same order have been predicted for the complexes between formamide and HP. In these systems, the most stable structure has been found when HP accepts a proton from the  $\text{NH}_2$  group while donating a proton to the  $\text{C}=\text{O}$  bond and the less stable structure has been predicted when both O atoms of HP are acting as proton acceptor [15].

It is also worth to notice that for a given structure, the binding energies are not very sensitive to the nature of the halogen implanted on the ethenes. In a recent study on the complexes between the same ethene derivatives and water [18], we have shown that the acidity of the CH bond in the  $\text{CH(X)}$  group increases in the order



In the present complexes, the intermolecular  $\text{C1H5} \cdots \text{O}$  distances decrease in the same order. In the B complexes as for example, the  $\text{H5} \cdots \text{O}$  distance is equal to 2.499 Å in the  $\text{CH}_2=\text{CHF} \cdot \text{HP}$  complex and 2.382 Å in the  $\text{CH}_2=\text{CHBr}$  complex. The near-constant value of the binding energies in a given structure can be explained by the larger acceptor ability of the F atoms as compared with the Cl and Br ones. This is consistent with the NBO charges on the X atoms that will be discussed in Section 3. It has also been shown that the acceptor ability of the X atom correlates well with its electronegativity [23].

The complexes between monohalogenated ethenes and water, investigated in a recent work at the same level of theory are somewhat weaker [18]. The binding energy in the  $\text{H}_2\text{C}=\text{CHF} \cdot \text{H}_2\text{O}$  (AK) complex is  $-6.8 \text{ kJ mol}^{-1}$  as compared with the actual value of  $-8.1 \text{ kJ mol}^{-1}$  for the  $\text{H}_2\text{C}=\text{CHF} \cdot \text{H}_2\text{O}_2$  system. The  $\text{H8} \cdots \text{F}$  distance is longer (2.146 Å) in the  $\text{H}_2\text{O}$  complex than in the HP complex (2.083 Å). This reflects the larger proton donor ability of the OH group of HP. In contrast, the  $\text{H2} \cdots \text{O8}$  distance is shorter in the  $\text{H}_2\text{O}$  complex (2.477 Å) than in the HP one (2.614 Å) and this reflects the larger proton acceptor ability of the O atom of  $\text{H}_2\text{O}$  [24]. The same trend is also found for the complexes involving  $\text{H}_2\text{C}=\text{CHCl}$  and  $\text{CH}_2=\text{CHBr}$  (Fig. 1). Complexes between water and uracil [10] or cytosine [11] are stronger than the complexes with

$\text{H}_2\text{O}_2$ . Interestingly, in the  $\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$  complex, the electron densities at the bond critical point demonstrate that  $\text{H}_2\text{O}_2$  is more acidic than  $\text{H}_2\text{O}$  [7]. These differences indicate that the properties of the proton-donating groups have more impact on the hydrogen bond energies than properties of the proton-accepting groups. This has been demonstrated for several hydrogen-bonded systems [25–29].

#### 3.2. Variations of the intramolecular distances and vibrational frequencies

Changes of relevant intramolecular distances resulting from the interaction between  $\text{H}_2\text{C}=\text{CHX}$  and HP are reported in Table 2. Perusal of these data shows that in the A and AK complexes, the  $\text{C1H5}$  bonds not involved in the interaction are contracted while the bonded  $\text{C4H2}$  bonds are slightly elongated. In the B complexes, the  $\text{C1H5}$  bonds involved in the interaction are contracted while the other CH bonds remain almost unchanged. In the C complexes, where both  $\text{C1H5}$  and  $\text{C4H6}$  bonds are involved in the interaction, the contractions of the  $\text{C1H5}$  bonds are larger than the  $\text{C4H6}$  ones. These data show that the  $\text{CH(X)}$  bonds are more sensitive to complex formation than the two CH bonds of the  $\text{CH}_2$  group. In all the systems, the interaction with HP results in an elongation of the CX bonds, the elongation of the CF bond being larger than the elongation of the CCl or CBr bonds. The OO bonds are also contracted. As for the  $\text{H}_2\text{C}=\text{CHX} \cdot \text{H}_2\text{O}$  systems, the  $\text{C}=\text{C}$  distances are weakly sensitive to the interaction with HP. The OH distances in HP are elongated by 1.1–3.8 mÅ.

According to the negative intramolecular response (NIR) mechanism proposed by Karpfen and Kryachko [30,31], blue shifts of XH stretching frequencies have a common feature, viz., a negative intramolecular coupling between the CH bonds and the vicinal bonds. If the vicinal bond stretches upon complex formation (in the present case the CX bond), the negative coupling causes a shortening of the  $\text{C1H5}$  bond. The  $\text{C1X}$  distances are markedly different in the three monomers. Therefore, we have considered the relative increase of the  $\text{C1H5}$  and  $\text{C1X}$  distances with respect to the distances in the isolated monomers ( $r^0(\text{C1H5})$  and  $r^0(\text{C1X})$ ). The following correlation illustrated in Fig. 2 is calculated:

$$\Delta r(\text{C1H5})/r^0(\text{C1H5}) = 0.19 - 0.136\Delta r(\text{C1X})/r^0(\text{C1X}) \quad (r = 0.946) \quad (1)$$

In order to avoid a coupling between the  $\nu(\text{CH})$  modes, the  $\nu(\text{CH})$  vibrational frequencies and IR intensities have been calculated in the partially deuterated isotopomers, namely  $\text{H2D6C4}=\text{CD5X}$  for the A and AK complexes and  $\text{D2D6C4}=\text{C1H5X}$  for the B and BK complexes. The frequency shifts of the CH and OH stretching vibrations along with the variations of their IR intensities are listed in Table 3.

Significant blue shifts between 5 and  $25 \text{ cm}^{-1}$  are predicted for the  $\nu(\text{C1H5})$  vibrations in the B and BK systems where the  $\text{C1H5}$  bond is involved in the interaction and between 4 and  $15 \text{ cm}^{-1}$  in the A and AK systems, in agreement with the smallest contraction of these bonds. Blue shifts of the  $\nu(\text{C1H5})$  vibration of ca.  $20 \text{ cm}^{-1}$  are also predicted for the C complexes. Small shifts, between  $-4$  and  $+4 \text{ cm}^{-1}$ , are predicted for the  $\nu(\text{C4H2})$  vibrations, showing that these vibrations cannot be categorized as blue- or red-shifted vibrations. Because of the known limitations of computational frequencies, frequency shifts can be in either directions, especially for weak interactions. The following correlation holds for all the CH bonds, the bonded as well as the non-bonded ones:

$$\Delta \nu(\text{CH}) = 3.1 - 12.8\Delta r(\text{CH}) \quad (r = 0.947) \quad (2)$$

For most of the blue-shifted hydrogen bonds, the interaction results in a decrease of the IR intensity of the  $\nu(\text{CH})$  vibration. For the present systems, no definitive trend can be extracted from our calcula-

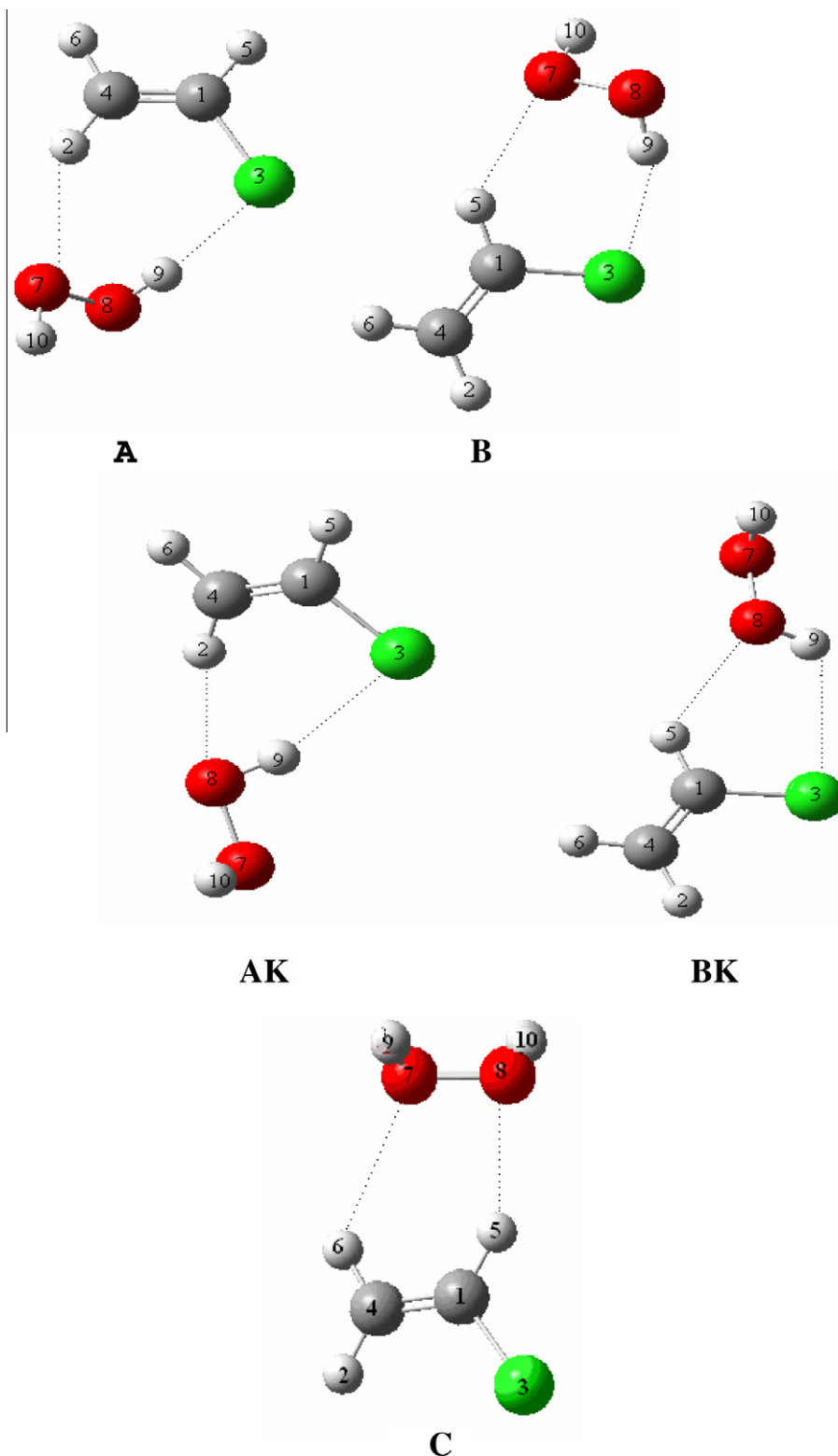


Fig. 1. MP2/6-31++G(d,p) optimized structure of the complexes between  $\text{CH}_2=\text{CHX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) and  $\text{H}_2\text{O}_2$ .

tions. In the partially deuterated isotopomers, the IR intensities of the  $\nu(\text{C4H2})$  and  $\nu(\text{C4H6})$  vibrations in the isolated molecules are very weak, between 0.2 and 0.9  $\text{km mol}^{-1}$ . When the  $\text{C4H2}$  group is bonded (A and AK complexes), the IR intensity increases. The IR intensity of the  $\nu(\text{C1H5})$  vibration fluctuates in both directions. Interestingly, the  $\nu(\text{C4H6})$  vibration becomes virtually IR inactive in the C complexes.

All the  $\nu(\text{OH})$  vibrations are red-shifted and their IR intensities increase. The red shifts are moderate as compared with hydrogen bonds of medium strength ( $200\text{--}500\text{ cm}^{-1}$ ) [32,33] and this reflects the weakness of the interaction. The red shifts range between 14 and 36  $\text{cm}^{-1}$  for the  $\text{CH}_2=\text{CHF} \cdot \text{HP}$  complexes, between 9 and 58  $\text{cm}^{-1}$  for the  $\text{CH}_2=\text{CHCl}$  complexes and between 30 and 73  $\text{cm}^{-1}$  for the  $\text{CH}_2=\text{CHBr}$  ones. As discussed in Section 1, the

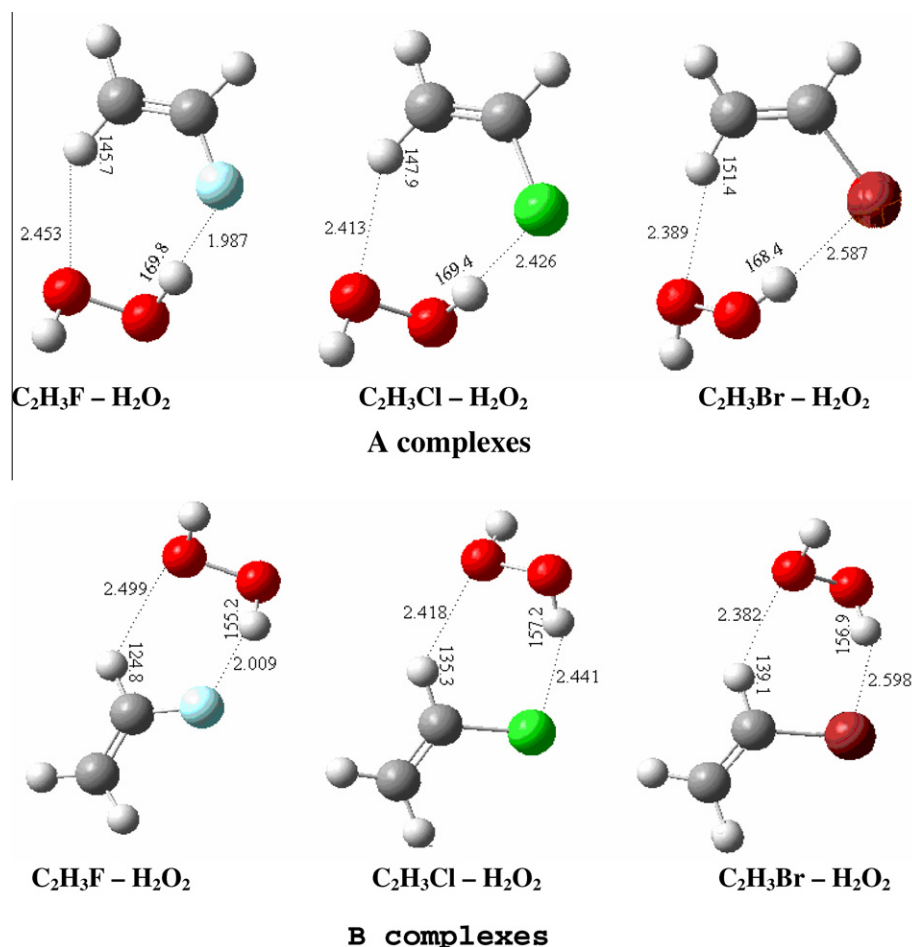


Fig. 1 (continued)

OH...F bonds are likely to be stronger than the OH...Cl or OH...Br bonds. Despite this fact, the frequency shifts of the corresponding  $\nu(\text{OH})$  vibrations are larger for the two systems. This apparent anomaly can be explained by the fact that, in neutral OH...X hydrogen bonds characterized by the same binding energies, the frequency shifts  $\Delta\nu(\text{OH})$  are much lower for the OH...F than for the OH...Cl or OH...Br bonds [34]. As shown for numerous hydrogen-bonded systems, correlations between hydrogen bond energies and frequency shifts strongly depend on the nature of the bond.

The  $\nu(\text{OH})$  frequency shifts ( $\text{cm}^{-1}$ ) are linearly correlated to the elongation of the OH bond ( $\text{\AA}$ ):

$$\Delta\nu(\text{OH}) = 18.6 - 23.50\Delta r(\text{OH}) \quad (r = 0.981) \quad (3)$$

The slope of Eq. (3) is larger than that of Eq. (2) indicating a greater sensitivity to variations of the corresponding bond lengths.

Our calculations predict an increase of the IR intensities of the  $\nu(\text{OH})$  vibrations by 6–155  $\text{km mol}^{-1}$ . These increases are very roughly proportional to the frequency shifts, the smallest increase of 6  $\text{km mol}^{-1}$  being calculated for the  $\text{H}_2\text{C}=\text{CHCl} \cdot \text{HP}$  complex ( $\Delta\nu = -11 \text{ cm}^{-1}$ ) and the largest increase of 155  $\text{km mol}^{-1}$  being calculated for the  $\text{H}_2\text{C}=\text{CHBr} \cdot \text{HP}$  system ( $\Delta\nu = -72 \text{ cm}^{-1}$ ).

### 3.3. NBO analysis

In this section, more attention will be paid to the changes in the NBO parameters related to the CHX part of the  $\text{H}_2\text{C}=\text{CHX}$  deriva-

tives which are, as discussed in Section 2, the most sensitive to the interaction with HP. Changes of the parameters of the OH bond of HP will be also discussed. Tables 4–6 report relevant NBO parameters namely the NBO charges, occupation of relevant  $\sigma^*$  antibonding orbital and the intramolecular hyperconjugation energies from the X lone pairs to the  $\sigma^*(\text{C1H5})$  orbitals. These parameters are indicated for the isolated molecules along with their changes resulting from the interaction with HP. These tables also contain the intermolecular hyperconjugation energies from the X lone pairs to the  $\sigma^*(\text{O8H9})$  orbitals in all the complexes or from the O lone pairs of HP to the  $\sigma^*(\text{C1H5})$  orbitals in the B and BK complexes.

In a first step, we want to discuss briefly the NBO data for the monomers. In a recent work, the importance of rehybridization in a variety of chemical phenomena has been outlined [35]. In ethene derivatives, a correlation was found between the s-character of C in CH5 and an inverse correlation between the s-character of the C in CX and the electronegativity of X (X = H,  $\text{BH}_2$ ,  $\text{CH}_3$ ,  $\text{NH}_2$ , OH, F). In order to test the validity of this correlation for the  $\text{CH}_2=\text{CHCl}$  and  $\text{CH}_2=\text{CHBr}$  molecules, we have also calculated at the MP2/6-311++G(3df,2p) level, the s-character of C at H in non-substituted ethene. We have found a value of 29.7% which is very similar to the value of 30.2% calculated at the B3LYP/6-31G(d,p) level in Ref. [33]. In  $\text{CH}_2=\text{CHBr}$ , the s-character of C at H5 is larger (32.1%) and the s-character of C at X is lower (24.6%) than those predicted from the electronegativity of X (H = 2.2, Br = 2.8, Cl = 3, F = 4). As discussed in several works [36–39], bonds from higher elements may have a higher p-character.

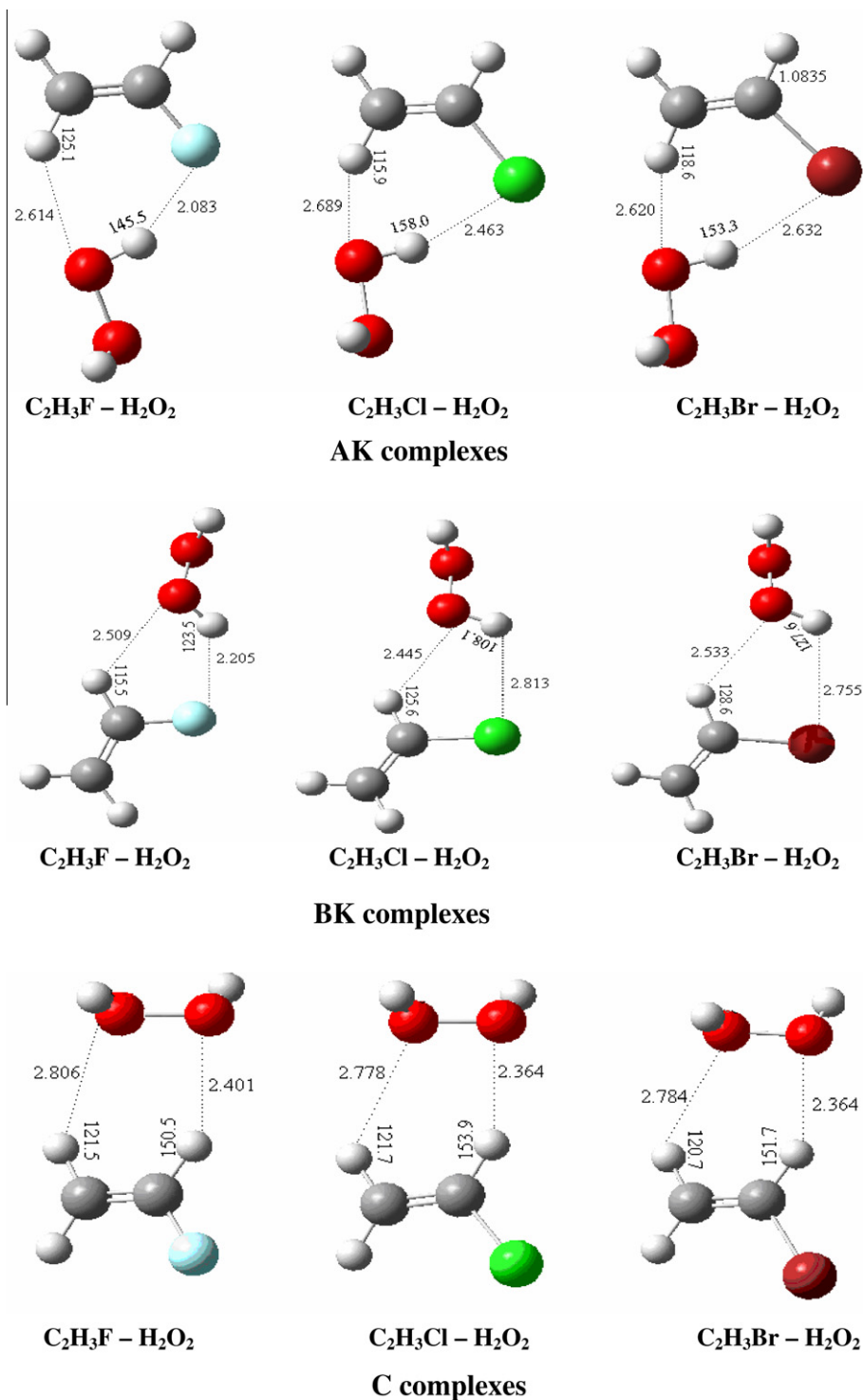


Fig. 1 (continued)

As expected for weak complexes, the charge transfer from one molecule to the other one is moderate and does not exceed 6 me. In all the complexes, except the C ones, the  $\text{CH}_2=\text{CHX}$  molecules act as electron donors toward the HP molecule.

As indicated in Tables 4–6, there is in all the complexes an increase of the polarity of the C1H5 bond. The increase of positive charge on the H5 atom is larger in the B and BK complexes where the C1H5 bond is involved in the interaction with HP. The increase of the positive charge on H5 is between 16 and 27 me as compared with the values between 3 and 7 me in the A and AK systems. The

**Table 1**

Hydrogen bond energies ( $-\Delta E_{\text{HB}}$ ) ( $\text{kJmol}^{-1}$ ) including ZPE- and BSSE-corrections for the complexes between  $\text{CH}_2=\text{CHX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ) and  $\text{H}_2\text{O}_2$ .<sup>a</sup>

Complex	$\text{CH}_2=\text{CHF} \cdot \text{H}_2\text{O}_2$	$\text{CH}_2=\text{CHCl} \cdot \text{H}_2\text{O}_2$	$\text{CH}_2=\text{CHBr} \cdot \text{H}_2\text{O}_2$
A	11.1 (4.7; 3.6)	10.2 (4.8; 4.4)	11.1 (4.2; 3.2)
B	11.6 (4.3; 3.6)	11.3 (4.5; 4.4)	12.2 (4.1; 3.4)
AK	8.1 (4.0; 2.7)	7.3 (4.4; 3.6)	8.0 (3.9; 2.7)
BK	8.7 (3.5; 2.7)	8.7 (2.9; 3.1)	9.1 (2.9; 3.4)
C	6.2 (3.4; 2.6)	6.5 (3.6; 3.0)	6.8 (3.4; 2.8)

<sup>a</sup> The values in parentheses correspond to the ZPE- and BSSE-corrections.



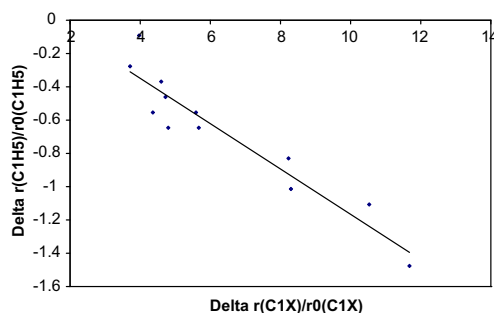
**Table 2**

Varations of relevant intramolecular distances (mÅ) in complexes between  $\text{CH}_2=\text{CHX}$  (X = F, Cl, Br) and  $\text{H}_2\text{O}_2$ .<sup>a,b</sup>

Complex	$\Delta r$	$\text{CH}_2=\text{CHF} \cdot \text{H}_2\text{O}_2$	$\text{CH}_2=\text{CHCl} \cdot \text{H}_2\text{O}_2$	$\text{CH}_2=\text{CHBr} \cdot \text{H}_2\text{O}_2$
A	$\Delta r(\text{C1H5})$	−1.2	−0.6	−0.4
	<b><math>\Delta r(\text{C4H2})</math></b>	<b>+0.5</b>	<b>+0.2</b>	<b>+0.1</b>
	$\Delta r(\text{C1X})$	+14.2	+9.7	+8.7
	$\Delta r(\text{OO})$	−1.1	−1.8	−2.0
	$\Delta r(\text{O8H9})$	+2.6	+3.1	+3.8
B	<b><math>\Delta r(\text{C1H5})</math></b>	<b>−1.6</b>	<b>−0.7</b>	<b>−0.5</b>
	$\Delta r(\text{C1X})$	+14.4	+9.8	+9.0
	$\Delta r(\text{OO})$	−0.7	−1.7	−1.9
	$\Delta r(\text{O8H9})$	+2.6	+3.2	+3.9
	<b><math>\Delta r(\text{C4H2})</math></b>	<b>+0.5</b>	<b>+0.3</b>	<b>+0.2</b>
AK	$\Delta r(\text{C1H5})$	−1.1	−0.6	−0.3
	$\Delta r(\text{C1X})$	+11.2	+7.5	+7.0
	$\Delta r(\text{OO})$	−0.8	−0.3	0
	$\Delta r(\text{O8H9})$	+1.7	+2.1	+2.6
	<b><math>\Delta r(\text{C1H5})</math></b>	<b>−0.9</b>	<b>−0.7</b>	<b>−0.1</b>
BK	$\Delta r(\text{C1X})$	+11.1	+8.3	+7.5
	$\Delta r(\text{OO})$	−1.2	−1.0	−0.6
	$\Delta r(\text{O8H9})$	+1.5	+1.1	+2.1
	$\Delta r(\text{C1H5})$	−1.1	−1.2	−1.0
	$\Delta r(\text{C4H6})$	−0.4	−0.3	−0.2
C	$\Delta r(\text{C1X})$	+4.3	+4.6	+4.5
	$\Delta r(\text{OO})$	−0.5	−0.4	−0.3

<sup>a</sup> In the isolated molecules, the  $r(\text{C1H5})$ ,  $r(\text{C4H2})$  and  $r(\text{C4H6})$  values are 1.0840, 1.0828, 1.0820 Å (X = F), 1.836, 1.0838, 1.0842 Å (X = Cl), 1.0838, 1.0840, 1.0853 Å (X = Br). The  $r(\text{C1X})$  distances are 1.348 Å (X = F), 1.729 Å (X = Cl) and 1.888 Å (X = Br). The  $r(\text{OH})$  distance in isolated  $\text{H}_2\text{O}_2$  is 0.9646 Å.

<sup>b</sup> The bold characters, indicate the CH bond involved in the interaction with  $\text{H}_2\text{O}_2$ .



**Fig. 2.**  $\Delta r(\text{C1H5})/r^0(\text{C1H5})$  as a function of  $\Delta r(\text{C1X})/r^0(\text{C1X})$ .

data are in agreement with the Bent's rule [40]. In all the systems, the interaction with HP results in a decrease of the  $\sigma^*(\text{C1H5})$  occupation, showing that both the hybridization and decrease of  $\sigma^*(\text{CH5})$  occupation contribute to the contraction of the C1H5 bond, in agreement with the considerations of Alabugin et al. [41]. The increase of s-character on the C at H5 is markedly larger in the B and BK complexes. As indicated in Table 2, the contraction of the C1H5 bond is larger for the  $\text{CH}_2=\text{CHF} \cdot \text{H}_2\text{O}_2$  complexes. This indicates that these complexes are more sensitive to variations in hybridization and  $\sigma^*$  occupation than the  $\text{CH}_2=\text{CHCl} \cdot \text{H}_2\text{O}_2$  and  $\text{CH}_2=\text{CHBr} \cdot \text{H}_2\text{O}_2$  systems.

As indicated in Table 4, the isolated molecules are stabilized by an intramolecular hyperconjugation energies from the sum of the X lone pairs to the  $\sigma^*(\text{C1H5})$  orbitals. These energies decrease in the complexes and there is in the B and BK complexes, an intermolecular hyperconjugation energy from the O lone pairs to the  $\sigma^*(\text{C1H5})$  orbitals or  $\sigma^*(\text{C4H6})$  orbitals in the C complexes. In order to compare the intra- and intermolecular hyperconjugation energies, it is useful to consider the  $R_E$  index [42,43] defined as the following ratio:

**Table 3**

Varations of the  $\nu(\text{CH})$  and  $\nu(\text{OH})$  stretching vibrations ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ , in parentheses) in complexes between  $\text{H}_2\text{C}=\text{CHX}$  (X = F, Cl, Br) and  $\text{H}_2\text{O}_2$ .<sup>a</sup>

Complex	$\Delta \nu(\text{CH/OH})$	$\text{H}_2\text{C}=\text{CHF} \cdot \text{H}_2\text{O}_2$	$\text{H}_2\text{C}=\text{CHCl} \cdot \text{H}_2\text{O}_2$	$\text{H}_2\text{C}=\text{CHBr} \cdot \text{H}_2\text{O}_2$
A	$\Delta \nu(\text{C1H5})$	+15(+0.5)	+8(+0.6)	+5(−0.7)
	$\Delta \nu(\text{C4H2})$	−2(+9)	+4(+6)	+4(+10)
	$\Delta \nu(\text{O8H9})$	−34(+136)	−56(+141)	−72(+155)
B	$\Delta \nu(\text{C1H5})$	+25(−1)	+15(+9)	+13(+14)
	$\Delta \nu(\text{O8H9})$	−36(+132)	−58(+139)	−73(+148)
AK	$\Delta \nu(\text{C1H5})$	+14(−1.5)	+8(−1.7)	+4(−1.1)
	$\Delta \nu(\text{C4H2})$	−4(+1.6)	−1(+0.7)	0(+1.3)
	$\Delta \nu(\text{O8H9})$	−16(+72)	−36(+112)	−48(+112)
BK	$\Delta \nu(\text{C1H5})$	+16(−4)	+15(+6)	+5(+8)
	$\Delta \nu(\text{O8H9})$	−14(+33)	−9(+6)	−30(+39)
C	$\Delta \nu(\text{C1H5})$	+20(−6)	+22(+2)	+18(+7)
	$\Delta \nu(\text{C4H6})$	+6(−0.2)	+6(−0.7)	+5(−0.8)

<sup>a</sup> The  $\nu(\text{CH})$  frequencies ( $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ ) of the  $\nu(\text{C1H5})$  vibration in isolated  $\text{H}_2\text{C}=\text{CHX}$  are: 3257 (7) (X = F), 3249 (6) (X = Cl), 3247 (5) (X = Br). The same parameters for the  $\nu(\text{C4H2})$  vibration are 3270 (0.9) (X = F), 3255 (0.4) (X = Cl), 3253 (0.2) (X = Br) and for the  $\nu(\text{C4H6})$  vibration (3277 (0.6) (X = F), 3250 (0.7) (X = Cl), 3238 (0.8) (X = Br). The average of the  $\nu^{\text{as}}$  and  $\nu^{\text{s}}$ (OH) vibrations in isolated  $\text{H}_2\text{O}_2$  is 3848  $\text{cm}^{-1}$  and the average IR intensity is 43  $\text{km mol}^{-1}$ .

**Table 4**

NBO data for the  $\text{CH}_2=\text{CHF} \cdot \text{H}_2\text{O}_2$  complexes. NBO charges (e),  $\sigma^*$  occupation (me), % s-character of C1(H5), intramolecular hyperconjugation energies ( $\text{kJ mol}^{-1}$ ) in isolated  $\text{CH}_2=\text{CHF}$  and variations resulting from the interaction with  $\text{H}_2\text{O}_2$ . Charge transfer (me) and intermolecular hyperconjugation energies ( $\text{kJ mol}^{-1}$ ).

$\text{H}_2\text{C}=\text{CHF}$	Isolated	A	B	AK	BK	C
$q(\text{C1})$	0.328	+23 <sup>a</sup>	+16	+19	+13	+7
$q(\text{H5})$	0.149	−7	−26	−7	−23	−21
$q(\text{F})$	−0.410	+23	+23	+18	+19	+7
CT		3 <sup>b</sup>	2 <sup>b</sup>	2 <sup>b</sup>	3 <sup>b</sup>	5 <sup>c</sup>
$\sigma^*(\text{C1H5})$	20.5	−1.3	−1.2	−1.1	−0.9	+0.5
$\sigma^*(\text{C1F3})$	21.0	+3.0	+2.2	+2.2	+1.7	+0.5
% s (C1H5)	32.3	+0.5	+1.0	+0.5	+0.8	+0.8
% s (C1F3)	23.1	−0.7	−0.9	−0.6	−0.7	−0.3
$\Sigma \text{LPF} \rightarrow \sigma^*(\text{C1H5})$	36.3	−2.7	−6.0	−1.9	−5.8	−2.7
$\Sigma \text{LPF} \rightarrow \sigma^*(\text{O8H9})$		18.4	16.2	9.8	3.9	
$\text{LPO8} \rightarrow \sigma^*(\text{C1H5})$			3.1		3.0	7.3
$\text{LPO7} \rightarrow \sigma^*(\text{C4H6})$						0.9
$\sigma^*(\text{OH})$	3.2	+6.3	+5.5	+3.6	+1.8	+0.1
% s (OH)	22.6	+1.6	+1.4	+1.2	+0.8	
$R_E$			1.94		1.90	0.37

<sup>a</sup> Positive and negative signs indicate increase of decrease of electronic charge.

<sup>b</sup> Charge transfer from  $\text{CH}_2=\text{CHX}$  to HP.

<sup>c</sup> Charge transfer from HP to  $\text{CH}_2=\text{CHX}$ .

$$R_E = \frac{\Delta E^{(2)}[\text{X} \rightarrow \sigma^*(\text{C1H5})]}{E^{\text{int}}[n_O \rightarrow \sigma^*(\text{C1H5})]}$$

where  $\Delta E^{(2)}$  is the difference between the intramolecular hyperconjugation in the monomer and in the complex and  $E^{\text{int}}$ , the intermolecular hyperconjugation energy. This ratio can be used to describe the strength of the electronic distribution effect. As indicated in Table 4, this ratio takes values between 1.90 and 1.94 for the  $\text{CH}_2=\text{CHF}$  complexes and is markedly lower for the two other systems where this ratio comprises between 1 and 1.23. In the C complexes where both O atoms of HP participate to the intermolecular charge transfer, the  $R_E$  ratio is still lower, between 0.26 and 0.37. As discussed in a recent work [43], the larger the electron density in the  $\sigma^*$  orbital of the proton acceptor, the stronger the electron distribution in the complex. This does not seem to be the case in the present systems where the  $\sigma^*(\text{C1H5})$  occupation is the lowest in the  $\text{CH}_2=\text{CHF}$  monomer (20.5 me) and the largest in the  $\text{CH}_2=\text{CHCl}$  monomer (23.6 me). The largest  $R_E$  value in the  $\text{CH}_2=\text{CHF} \cdot \text{H}_2\text{O}_2$  system can be explained by the values of the intermolecular hyper-

**Table 5**  
NBO parameters for the  $\text{CH}_2=\text{CHCl} \cdot \text{H}_2\text{O}_2$  complexes.<sup>a</sup>

$\text{H}_2\text{C}=\text{CHCl}$	Isolated	A	B	AK	BK	C
$q(\text{C1})$	−0.180	+13	+4	+13	−3	+1
$q(\text{H5})$	0.190	−4	−16	−4	−23	+21
$q(\text{Cl})$	−0.034	+22	+25	+15	+23	+15
CT		6 <sup>b</sup>	6 <sup>b</sup>	6 <sup>b</sup>	1 <sup>c</sup>	5 <sup>c</sup>
$\sigma^*(\text{C1H5})$	23.6	−0.9	−0.9	−0.5	−0.7	0
$\sigma^*(\text{C1Cl3})$	20.1	+2.1	+1.5	+1.8	+1.4	+0.9
%s(C1H5)	31.6	+0.5	+1.2	+0.4	+0.9	+1.0
%s(C1Cl3)	25.0	−0.7	−1.1	−0.5	−0.8	−0.5
$\Sigma\text{LPCl} \rightarrow \sigma^*(\text{C1H5})$	35.4	−4.3	−5.9	−1.7	−3.8	−2.6
$\Sigma\text{LPCl} \rightarrow \sigma^*(\text{O8H9})$		19.2	18.1	14.5	1.1	
$\text{LP08} \rightarrow \sigma^*(\text{C1H5})$			4.8		3.5	7.8
$\text{LP07} \rightarrow \sigma^*(\text{C4H6})$						1.1
$\sigma^*(\text{OH})$	3.2	+8.3	+7.7	+6.4	+0.8	+0.1
%sO(H)	22.6	+1.6	+1.4	+1.2	+0.5	
$R_E$			1.23		1.09	0.29

<sup>a</sup> Positive and negative signs indicate increase of decrease of electronic charge.

<sup>b</sup> Charge transfer from  $\text{CH}_2=\text{CHX}$  to HP.

<sup>c</sup> Charge transfer from HP to  $\text{CH}_2=\text{CHX}$ .

**Table 6**  
NBO parameters for the  $\text{CH}_2=\text{CHBr} \cdot \text{H}_2\text{O}_2$  complexes.<sup>a</sup>

$\text{H}_2\text{C}=\text{CHBr}$	Isolated	A	B	AK	BK	C
$q(\text{C1})$	−0.265	+10	+1	+11	−1	+21
$q(\text{H5})$	0.195	−3	−27	−3	−22	−22
$q(\text{Br})$	0.034	+24	+27	+17	+25	+15
CT		6 <sup>b</sup>	5 <sup>b</sup>	5 <sup>b</sup>	1 <sup>b</sup>	5 <sup>c</sup>
$\sigma^*(\text{C1H5})$	21.5	−0.6	−0.7	−0.5	−0.9	−0.2
$\sigma^*(\text{C1Br})$	22.2	+2.4	+2.7	+1.7	+1.4	+1.2
%s(C1H5)	32.1	+0.4	+1.2	+0.3	+0.9	+0.9
%s(C1Br3)	24.6	−0.7	−1.3	−0.5	−1.0	−0.7
$\Sigma\text{LPBr} \rightarrow \sigma^*(\text{C1H5})$	28.1	−3.9	−5.3	−1.2	−3.5	−2.1
$\Sigma\text{LPBr} \rightarrow \sigma^*(\text{O8H9})$		18.3	17.6	12.4	6.0	
$\text{LP08} \rightarrow \sigma^*(\text{C1H5})$			5.3		3.2	7.2
$\text{LP07} \rightarrow \sigma^*(\text{C4H6})$						1.1
$\sigma^*(\text{OH})$	3.2	+8.7	+8.0	+6.2	+4.1	+0.1
%sO(H)	22.6	+1.5	+1.3	+1.3	+0.8	
$R_E$			1.0		1.09	0.26

<sup>a</sup> Positive and negative signs indicate increase of decrease of electronic charge.

<sup>b</sup> Charge transfer from  $\text{CH}_2=\text{CHX}$  to HP.

<sup>c</sup> Charge transfer from HP to  $\text{CH}_2=\text{CHX}$ .

conjugation energies (3 kJ mol<sup>−1</sup>) which are lower than in the other complexes (between 3.2 and 5.3 kJ mol<sup>−1</sup>). This is in good agreement with the lower acidity of the C1H5(F) bond. Also, the OH...F bond is stronger than the OH...Br bond, the NBO charges on the F and Br atoms being −0.41 e and 0.03 e, respectively. This is in agreement with the geometric data discussed in Section 1.

The variations of charges on the bonded  $\text{H}_2\text{O}_2$  molecules are also worth mentioning. The interaction with the  $\text{CH}_2=\text{CHX}$  molecules results in an asymmetry of the charges in  $\text{H}_2\text{O}_2$ . For the O8H9...F3 bond in the  $\text{CH}_2=\text{CHF}$  (A) complex as for example, the

H9 atom loses 22 me and the O8 atom gains 6 me; in the C4H2...O bond, the O atom gains 20 me and the H10 atom loses 1 me. These data shows that the interaction with HP induces a change of polarity of the bonds in HP. As previously stated, the overall charge transfer from  $\text{CH}_2=\text{CHF}$  to HP is weak and equal to 3 me. Similar results are found for the other AK, B and BK complexes. In the C complexes, the increase of the polarity of the O8H10 bond is larger than that of the O7H9 bond, reflecting again the stronger intermolecular C1H5...O8 bond as compared with the C4H6...O7 one.

Further, the elongations of the OH bond are roughly proportional to the occupation of the  $\sigma^*(\text{OH})$  orbitals:

$$\Delta r(\text{OH}) = 0.74 + 0.32\sigma^*(\text{OH}) \quad (r = 0.931) \quad (4)$$

It seemed to us interesting to discuss the correlation between the elongation of the OH bond (or its frequency shift) and the intermolecular hyperconjugation energies from the X lone pairs to the  $\sigma^*(\text{OH})$  orbitals. As shown in Fig. 3a and b, two separate correlations are obtained for the OH...F and OH...Cl bonds on one side and the OH...Br bonds on the other side. For the OH...F and OH...Cl bonds, we have obtained the following correlation:

$$\Delta r(\text{OH}) (\text{m}\text{\AA}) = 1.086 e^{0.053(E(2))} \quad (r = 0.970) \quad (5)$$

For the OH...Br bonds:

$$\Delta r(\text{OH}) (\text{m}\text{\AA}) = 1.484 e^{0.052E(2)} \quad (r = 0.980) \quad (6)$$

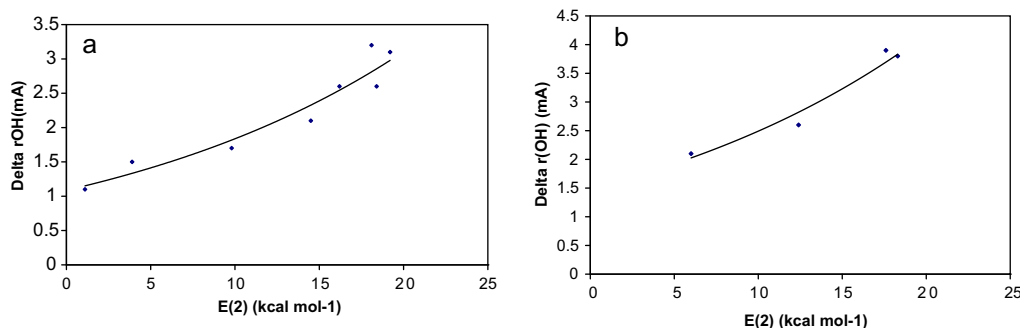
Comparison of Eqs. (5) and (6) shows that for the same  $E^{(2)}$  value, the elongation of the OH bond is markedly larger (by about 1 mÅ) for the OH...Br than for the OH...F or OH...Cl bonds. The same conclusion can be extracted from the frequency shifts of the  $\nu(\text{OH})$  vibrations. As outlined in Section 2, these frequency shifts are larger for the OH...Br than for the OH...F bonds.

The NBO charges on all the atoms in the isolated molecules and their adducts with HP are given in Supplementary data.

#### 4. Concluding remarks

In the present work, the complexes between monohalogenated ethenes  $\text{CH}_2=\text{CHX}$  (X = F, Cl, Br) and hydrogen peroxide are investigated theoretically at the MP2/6-31++G(3df,2p) level. The main conclusions of our work are:

- Several stable cyclic complexes characterized by OH...X and CH...O hydrogen bonds are found on the potential energy surface. The binding energies range between 7 and 12 kcal mol<sup>−1</sup>. Weaker complexes where both atoms of  $\text{H}_2\text{O}_2$  are acting as proton acceptors are also identified.
- The CH bonds participating to the interaction are contracted and the corresponding stretching vibrations blue-shifted. The results are discussed as a function of the  $\sigma^*(\text{CH})$  occupation and the hybridization of the C (H) atom.



**Fig. 3.**  $\Delta r(\text{OH})$  (mÅ) as a function of  $E^{(2)}(\text{LPX} \rightarrow \sigma^*(\text{OH}))$  (kcal mol<sup>−1</sup>). (a) OH...F and OH...Cl bonds. (b) OH...Br bonds.

3. The OH bonds are elongated and red-shifted.
4. The intra- and intermolecular hyperconjugation energies are discussed.
5. The geometric data and NBO parameters suggest that the strength of the CH...O hydrogen bonds is ordered according to  $\text{CH}_2=\text{CHF} < \text{CH}_2=\text{CHCl} < \text{CH}_2=\text{CHBr}$ . The OH...X hydrogen bonds follow an inverse order.

## Acknowledgements

The authors acknowledge the Ministry of Science and Technology of Vietnam (Project B2009-17-193) and Hanoi National University of Education (Project SPHN-08-261-TRIG).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.01.062.

## References

- [1] R.P. Wayne, Chemistry of Atmospheres, Clarendon Press, Oxford, 1991.
- [2] D.H. Zhang, J.Z. Zhang, J. Chem. Phys. 98 (1993) 6276.
- [3] M.S. Cooper, H. Heaney, A. Newbold, W.R. Sanderson, Synlett (1990) 533.
- [4] M. Fontecavé, J.L. Pierre, Bull. Chim. France 128 (1991) 505.
- [5] Y. Abe, S. Okada, R. Naka, R. Horii, S. Inoue, S. Taniguchi, S.J. Yamabé, J. Chem. Soc., Perkin Trans. 2 (1992) 2221.
- [6] J.A. Dobado, J. Molina, J. Phys. Chem. 98 (1994) 1819.
- [7] X.-H. Ju, J.-J. Xiao, H.-M. Xiao, J. Mol. Struct. 626 (2003) 231.
- [8] J.A. Dobado, J. Molina, J. Phys. Chem. 98 (1994) 7819.
- [9] J.A. Dobado, J. Molina, J.J. Portal, J. Phys. Chem. A 102 (1998) 778.
- [10] J.A. Dobado, J. Molina, J. Phys. Chem. A 103 (1999) 4755.
- [11] R. Wyzokiński, D. Michalska, D.C. Bieñko, Th. Zeegers-Huyskens, J. Phys. Chem. A 107 (2003) 8730.
- [12] R. Wyzokiński, D. Bienko, D. Michalska, Th. Zeegers-Huyskens, Chem. Phys. 315 (2005) 17.
- [13] H.M.T. Nguyen, M.T. Nguyen, J. Peeters, Th. Zeegers-Huyskens, J. Phys. Chem. A 108 (2004) 11101.
- [14] H.M.T. Nguyen, J. Peeters, Th. Zeegers-Huyskens, J. Mol. Struct. 792 (2006).
- [15] D.-m. Du, A.-p. Fu, Z.-y. Zhou, J. Mol. Struct. (THEOCHEM) 731 (2005) 49.
- [16] M. Solimannejad, S. Scheiner, Chem. Phys. Lett. 429 (2006) 38.
- [17] G. Zhang, A. Yin, D. Chen, Int. J. Quantum Chem. 109 (2009) 920.
- [18] H.M.T. Nguyen, P.N. Diep, Th. Zeegers-Huyskens, J. Mol. Struct. (THEOCHEM) 897 (2009) 48.
- [19] M.J. Frisch et al., GAUSSIAN-03, Revision B.03, Gaussian Inc., Pittsburgh, PA, 2003.
- [20] S.F. Boys, F. Bernardi, Mol. Phys. 19 (1979) 553.
- [21] A.E. Rich, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
- [22] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37B (1988) 785.
- [23] V.I. Alabugin, T.A. Zeidan, J. Am. Chem. Soc. 124 (2002) 3175.
- [24] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988). The deprotonation enthalpies of the OH group of  $\text{H}_2\text{O}$  and HP are 1636 and 1573  $\text{kJ mol}^{-1}$ . The proton affinities of the O atoms of  $\text{H}_2\text{O}$  and HP are 697 and 678  $\text{kJ mol}^{-1}$ .
- [25] A.K. Chandra, M.T. Nguyen, T. Uchimaru, Th. Zeegers-Huyskens, J. Phys. Chem. A 103 (1999) 8853.
- [26] A.K. Chandra, T. Uchimaru, Th. Zeegers-Huyskens, J. Mol. Struct. 605 (2002) 213.
- [27] A.K. Chandra, Th. Zeegers-Huyskens, J. Phys. Chem. A 109 (2005) 12006.
- [28] L.J. Bian, J. Phys. Chem. A 107 (2003) 11517.
- [29] R. Zybalyuk, O.V. Shishkin, L. Gorb, J. Leszczynski, J. Phys. Chem. A 113 (2009) 2943.
- [30] A.K. Karpfen, E.S. Kryachko, Chem. Phys. 310 (2005) 77.
- [31] A.K. Karpfen, E.S. Kryachko, Chem. Phys. Lett. 431 (2006) 428.
- [32] M.D. Joesten, L.J. Schaad, Hydrogen Bonding, Marcel Dekker, New York, 1974.
- [33] P.L. Huyskens, W.A.P. Luck, Th. Zeegers-Huyskens, Intermolecular Forces. An Introduction to Modern Methods and Results, Springer, Berlin, 1991.
- [34] For the complexes between phenol and  $\text{C}_6\text{H}_{11}\text{X}$  as for example, the binding energies are 2.84 ( $\text{X}=\text{F}$ ), 1.95 ( $\text{X}=\text{Cl}$ ) and 1.78 ( $\text{X}=\text{Br}$ )  $\text{kcal mol}^{-1}$ . The corresponding frequency shifts  $\Delta\nu(\text{OH})$  are equal to 53, 66 and 82  $\text{cm}^{-1}$ . These results indicate that for a binding energy of 1  $\text{kcal mol}^{-1}$ , the frequency shifts are approximately equal to 18 ( $\text{X}=\text{F}$ ), 34 ( $\text{X}=\text{Cl}$ ) and 46 ( $\text{X}=\text{Br}$ )  $\text{cm}^{-1}$  (from the results reported in Ref. [32]).
- [35] I.V. Alabugin, M. Manoharan, J. Comput. Chem. 28 (2007) 373.
- [36] W. Kutzelnigg, Angew. Chem., Int. Edn. Engl. 23 (1984) 272.
- [37] W. Kutzelnigg, J. Mol. Struct. (THEOCHEM) 169 (1988) 403.
- [38] M.H. Palmer, J. Mol. Struct. 405 (1997) 179.
- [39] M.H. Palmer, J. Mol. Struct. 405 (1997) 193.
- [40] H.A. Bent, Chem. Rev. 61 (1961) 275.
- [41] V. Alabugin, M. Manoharan, S. Peabody, F. Weinhold, J. Am. Chem. Soc. 125 (2003) 5973.
- [42] Y. Yang, W.J. Zhang, J. Mol. Struct. (THEOCHEM) 814 (2007) 113.
- [43] Y. Yang, Int. J. Quantum Chem. 109 (2009) 266.