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Stabilities and Properties of Complexes Pairing Hydroperoxyl Radical with Monohalomethanes

Mohammad Solimannejad*
Quantum Chemistry Group, Department of Chemistry, Arak University, 38156-879 Arak, Iran

Steve Scheiner
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

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UMP2/aug-cc-pvdz calculations are used to analyze the interaction between hydroperoxyl radical (HOO) and CH_3X (X = F, Cl, Br). Two minima are located on the potential energy surface of each complex. The more strongly bound contains a OH···X bond, along with CH···O; only CH···O bonds occur in the less stable minimum. Binding energies of the dominant minimum lie in the range of 20−24 kJ/mol, with X = F the most strongly bound. Analysis of the perturbations of the covalent bond lengths within each subunit caused by complexation, coupled with vibrational frequencies and charge transfers, opens a window into the nature of the interactions.

1. Introduction

The importance of noncovalent intermolecular interactions in many areas of contemporary chemical physics has been demonstrated in numerous studies of such systems.[1] From a fundamental point of view, the van der Waals complexes formed by these noncovalent interactions are significant in their own right, as they bridge the gap between the free molecular systems and the corresponding condensed phases. Noncovalently bonded molecular clusters are of a certain practical importance in many areas, such as atmospheric chemistry and catalysis, as well as in biochemically relevant processes. As an illustrative example related to the significance of noncovalent systems in atmospheric chemistry, the proposed mechanisms aiming to explain ozone layer depletion involve formation of certain intermolecular complexes (or clusters).[2−5] In order to be able to understand the details of the reactions occurring in atmospheric conditions, one should be first capable of understanding the structure, stability, and certain other properties of the intermolecular clusters taking part in these reactions.

Among all noncovalent interactions, the hydrogen bonding types are particularly significant. Although the term "hydrogen bond" is widely used, it seems that a precise definition of this phenomenon (accounting for all of its relevant aspects) has not yet been fully agreed upon. Although a rather large number of studies devoted to the hydrogen bonding phenomenon have been published (from both experimental and theoretical viewpoints[6,7]), most of these works have been devoted to hydrogen bonds formed in the case of complexes between neutral and ionic (usually closed-shell) systems on one hand, and closed-shell systems on the other. Studies of systems involving open-shell systems (such as radicals) are far more limited. This paucity is due to both experimental and theoretical difficulties arising in the description and characterization of the systems in question. Bearing in mind the importance of free radicals in a number of fields (e.g. atmospheric chemistry and life sciences), detailed information about the intermolecular interactions involving these open-shell systems is desirable.

The hydroperoxyl radical participates in numerous oxidation reactions.[8] Its interaction with various molecules influences the stabilization of newly formed hot radicals and may affect their reactivity. One of the more intriguing areas of radical−molecule complex studies arises from the discovery of the formation of surprisingly stable HO_2 complexes.[9] A number of related systems combining HO_2 with H_2O,[10] HNO_3,[11] H_2SO_4,[12] RC(O)OH (R = H, CH_3, CF_3),[13] $CF_3C(O)OH$,[14] HOC(O)OH,[15] RC(O)NH_2 (R = H, CH_3, NH_2),[16] SO_3,[17] NH_3,[18] HF,[19] and HCl[20] have been reported in the literature.

Noncovalently bonded complexes of CH_3X (X = F, Cl, Br) are of prime importance in atmospheric chemistry as many of the processes that degrade ozone involve halogen-containing species. In particular, methyl chloride and methyl bromide are important atmospheric trace gases (tropospheric mixing ratios of 12 and 600 pptv, respectively) that contribute directly to stratospheric ozone depletion.[21] Bearing in mind that the CH_3X species could be easily formed in the environment (e.g. important sources of CH_3Cl include oceanic emissions, biomass burning, tropical forests; tropical plants may also be important sources of natural CH_3Br[22]), and that species including a halogen atom are crucial for most ozone removal processes, the title complexes in the present study are of paramount interest in the field of atmospheric chemistry.

Despite the potential importance of both HOO and the halomethanes, to our best knowledge there is available in the literature neither theoretical nor experimental study of the possible interaction of a HOO radical with any of the monohalomethanes. In the absence of experimental information, a theoretical analysis of the potential existence of such complexes and their properties would appear to be in order.

Interestingly, both the HOO radical and CH_3X molecules act as both hydrogen bond donors and acceptors,[10−20,23−25] leading to a wealth of potential minima to be considered, not the least of which are cyclic structures. The work presented here not only

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* Corresponding author: m-solimannejad@araku.ac.ir.

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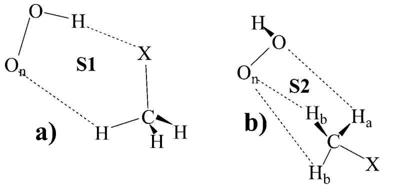

Figure 1. Geometries of optimized structures of complexes pairing CH_3X (X = F, Cl, Br) and HOO radical.

examines the structure and stability of the various complexes but also examines the fundamental features of the different sorts of interactions that are present. For example, the properties of OH···X bonds are compared with CH···O analogues, which include a weaker proton donor but a stronger acceptor.

2. Computational Details

Calculations were performed using the Gaussian03 system of codes.[26] The geometries of the isolated CH_3X (X = F, Cl, Br) and HOO moieties and their complexes were fully optimized at the UMP2/aug-cc-pvdz computational level. This method and basis set adequately describes hydrogen bonds and so is reliable for the purpose of our study. The modified GDIIS algorithm was implemented in productive searches for stationary points,[27] as it has been found to be effective in the cases of weak noncovalent intermolecular interactions.[16,17,28,29] Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of zero-point vibrational energies (ZPE). The counterpoise (CP) procedure[30] was used to correct the interaction energy for basis set superposition error (BSSE).

3. Results and Discussion

Two minima were identified on the potential energy surface of each complex. The more stable of the two, termed S1, is illustrated in Figure 1a to contain a pair of H-bonds. The first such bond connects the proton of OOH with the halogen acceptor atom. The CH of the CH_3X molecule acts as donor in the second bond, and the role of acceptor atom is played by the O of OOH that is not covalently bonded to the hydrogen, designated here as O_n. This complex is apparently quite insensitive to rotation of the CH_3X molecules about its C−X axis. Whereas the minima for the F and Br systems are as illustrated in Figure 1a, the minimum for OOH···CH_3Cl contains an approximate 60° rotation, such that there are a pair of CH···O H-bonds to the O atom of OOH, rather than a single one. The second sort of complex, S2, is also cyclic, but the halogen atom does not participate in either H-bond. The various protons of the CH_3X molecule are donated to the two O atoms of OOH, as indicated in Figure 1b.

The potential energy surface was scoured for other possible minima. For example, based on earlier calculations of the related complexes, pairing the CH_3X halides with the HOOH molecule,[23] or with HCOOH,[31] another minimum had been anticipated in the surface. This geometry is related to S1 in that it contains both an OH···X and a CH···O H-bond. It differs, however, in that both of these H-bonds involve the same O atom of the hydroxyl. However, optimization of this sort of structure quickly devolved into the S1 minimum, with no intervening energy barrier. Other structures examined as possible minima allowed a CH of the CH_3X to approach an O atom of OOH. Regardless of which O atom was approached, these structures also rotated around and fell into the S1 basin. Likewise, an attempt to form the OH···X bond without an accompanying CH···O also failed as the S1 minimum was adopted.

TABLE 1: Binding Energies (kJ mol^{-1}) and Thermodynamic Data for the Association of CH_3X (X = F, Cl, Br) with HOO Radical at the UMP2/aug-cc-pvdz Level

X	D_e	$D_e^{cp\ a}$	ΔE_0^{b}	$\Delta H(298)$
		S1		
F	−29.9	−24.4	−23.5	−23.2
Cl	−26.4	−20.0	−21.3	−20.4
Br	−27.7	−19.6	−22.7	−21.8
		S2		
F	−9.6	−5.7	−6.4	−4.3
Cl	−9.5	−5.7	−6.4	−4.2
Br	−9.6	−5.5	−6.9	−4.3

[a] D_e^{cp} refers to the interaction energy after counterpoise correction, D_e + BSSE. [b] ΔE_0 represents energy of complexation including ZPE.

TABLE 2: H-Bond Distances (*R*, in Å), Changes in Internal Bond Lengths (Δ*r*, in mÅ), and Charge Transfer (*q*, in me) Occurring upon Formation of the S1 Complex

	F	Cl	Br
R(OH···X)	1.795	2.269	2.419
R(CH···O_n)	2.602	2.953 2.967	2.484
Δr(OH)	6	7	7
Δr(CH)	−3	−2	−1
Δr(C−X)	22	10	8
Δr(O−O)	−4	−4	−5
$q(X \rightarrow OH)^a$	15	17	19
$q(O_n \rightarrow CH)^a$	1	0.5	3

[a] Charge transferred from lone pair to σ^*.

The energetics of the two sorts of complexes identified as minima on the surfaces are reported in Table 1 where it may be seen that the OOH···CH_3F complex is bound by 24.4 kJ/mol, following counterpoise correction. The interaction is weakened a bit for Cl and Br, for which $-\Delta E_0$ is computed to be 20 kJ/mol. The similarity of the binding energies of the Cl- and Br-containing S1 complexes is consistent with very recent results for the systems wherein OOH is replaced by HCOOH.[31]

Given the absence of the relatively strong OH···X bonds, it is not surprising to find that the S2 structures are much more weakly bound than S1. Indeed, the binding energies of the latter are roughly $^1/_4$ those of the former. The interaction of the CH_3 protons with the two O atoms, forming CH···O bonds only, makes the S2 structure similar to the weakly bound A3 minima identified in the potential energy surface of CH_3X with the anti rotamer of HCOOH;[31] this similarity extends to the interaction energies. The total binding energies of the S2 structures in Figure 1, just under 6 kJ/mol, are virtually independent of the nature of the halogen atom, as was true for the HCOOH analogues.[31]

Various aspects of the geometries of the S1 structures are reported in Table 2. The length of the upper OH···F H-bond is 1.795 Å, indicating a fairly strong interaction. This length of course, increases in the order F < Cl < Br as the halogen atom enlarges. In contrast, the length of the lower, and presumably weaker, CH···O_n bond is shorter for OOH···CH_3Br than for OOH···CH_3F, suggesting a strengthening. (The pair of bifurcated CH···O bonds in OOH···CH_3Cl are both longer, as both contain an angular distortion.) The next row of Table 2 indicates that the OH bond of OOH is lengthened upon formation of the complex, relative to the isolated OOH molecule, by some 6−7 mÅ, with little dependence upon the nature of the halogen atom. The CH bonds of the CH_3X molecule that form the H-bond with O_n are shortened by a smaller amount, 1−3 mÅ. This shortening diminishes in the order F > Cl > Br. A like trend is exhibited by the elongation of the C−X bond, which is as much as 22 mÅ for OOH···CH_3F. In contrast, the O−O bond length

TABLE 3: H-Bond Distances (*R*, in Å), Changes in Internal Bond Lengths (Δ*r*, in mÅ), and Charge Transfer (*q*, in me) Occurring upon Formation of the S2 Complex

	F	Cl	Br
$R(CH_a\cdots O)$	2.666	2.600	2.571
$R(CH_b\cdots O_n)$	2.960	3.070	3.117
$\Delta r(CH_a)$	−1	−1	−2
$\Delta r(CH_b)$	−1	−1	−1
$\Delta r(C-X)$	4	3	1
$q(O \rightarrow CH_a)$	0.4	0.5	0.6

TABLE 4: Harmonic Vibrational Frequencies (cm^{-1}) Computed for the S1 Complex at the UMP2/aug-cc-pvdz Level

	X = F	X = Cl	X = Br
	OOH		
O−O stretch	1246	1237	1237
OOH bend	1532	1508	1506
O−H stretch	3539	3511	3501
	CH_3X		
C−X stretch	982	728	619
bending motions	1181	1036	979
	1189	1039	989
	1465	1371	1322
	1485	1464	1461
	1494	1469	1470
CH stretch	3107	3154	3112
	3229	3240	3240
	3239	3246	3251
	Intermolecular		
	28	15	8
	53	62	78
CH···O stretch	114	97	116
	139	112	86
OH···X stretch	211	171	161
OOH torsion	473	402	383

TABLE 5: Changes in Internal Stretching Frequencies (cm^{-1}) Occurring within S1 $OOH\cdots CH_3X$ Complexes

$\Delta\nu$	F	Cl	Br
		OOH	
O−H	−103	−131	−141
O−O	49	40	40
		CH_3X	
CH	35	22	19
X−C	−53	−22	−13

of OOH is reduced by 4−5 mÅ, suggestive of a slight bond strengthening.

The final two rows of Table 2 report the amount of NBO charge that is transferred from the lone pair of the X/O proton acceptor atom to the σ^* antibonding orbital of the OH/CH donor. The data confirm the much stronger nature of the OH···X bond, as compared to CH···O, since the charge transfers associated with the former exceed those of the latter by an order of magnitude. It is also noted that the amount of OH···X transfer increases in the order F < Cl < Br. The above H-bond lengths, as well as bond stretches and contractions, and electronic charge shifts, are very similar to those calculated for the comparable $HCOOH\cdots CH_3X$ complexes,[31] supporting the notion that these quantities are characteristic of the OH···X and CH···O bonds, and not highly dependent upon any particular system.

Analogous data are reported in Table 3 for the S2 complexes. The single CH···O H-bonds involving the OH oxygen atom of OOH are significantly shorter than the pair of H-bonds to the other, O_n, atom. The greater length of the latter are likely due in part to their bifurcated nature. But they may also be weaker, as indicated by the small CH bond contractions of about 1 mÅ, as well as the low amount of charge transfer, well under 1 me.

The computed vibrational frequencies of all three S1 complexes are listed in Table 4. These values are listed with those corresponding to internal vibrations of the OOH subunit at the top, followed by those in the CH_3X subunit, and last by the intermolecular vibrations. As seen in the penultimate row of Table 4, there is a trend for the intermolecular stretching frequency that corresponds roughly to the OH···X H-bond to diminish in the order F > Cl > Br, from 211 to 171 to 161 cm^{-1}. The intermolecular stretching frequencies of the weaker CH···O bond are considerably smaller, at 114, 97, and 116 cm^{-1}, respectively, and obey no clear pattern. The final row of Table 4 displays the frequency that corresponds to a torsional motion of the OOH around the O−O axis. This quantity may be considered another measure of the strength of the OH···X H-bond and diminishes in the order F > Cl > Br.

Two of the intermolecular vibrational modes can be loosely associated with stretches of each of the two H-bonds, and a third involves a rotation of the OOH molecule that breaks the OH···X bond. These quantities indicate that the latter H-bond is strongest for $OOH\cdots CH_3F$ and weakest for $OOH\cdots CH_3Br$. On the other hand, the degree of O−H bond elongation in OOH caused by complexation does not indicate any appreciable difference in H-bond strength among the three complexes; the magnitude of the O−H stretching frequency red shift would suggest that the OH···X bond is strongest for $OOH\cdots CH_3Br$ and weakest for $OOH\cdots CH_3F$, opposite to other indicators.

The final issue to address concerns the changes in the internal vibrational frequencies of the individual subunits brought about by formation of the binary complex. These changes are displayed in Table 5 for the S1 complexes, where it is immediately apparent that the OH stretches of OOH shift to the red, and those of the CH donors of CH_3X to the blue. The magnitudes of the former are considerably larger than those of the latter, again consistent with the stronger nature of the OH···X bonds. It is interesting to note that as the magnitudes of the OH red shifts increase, going from F to Cl to Br, the blue shifts of the CH bonds diminish. The latter reduction of the CH blue shift is consistent with the trend observed in the analogous $HCOOH\cdots CH_3X$ complexes.[31] Consistent with the prior observation that complexation causes a contraction of the peroxyl O−O bond length, Table 5 shows the increasing frequency expected of a strengthened bond. Likewise, the lowered X−C stretching frequencies within the CH_3X molecule are consonant with a weakened bond, characteristic of this molecule in similar bonding patterns in other systems.[31]

In summary, there appear to be two minima on the potential energy surface of each $OOH\cdots CH_3X$ complex. Both are cyclic in that they contain multiple H-bonds. Clearly the more stable of the two is that which contains a OH···X H-bond as well as an apparently weaker CH···O. The interaction energy of this complex is computed to be 24 kJ/mol for $OOH\cdots CH_3F$, and diminishes to 20 kJ/mol for the Cl and Br analogues. These values are not affected in any major way by inclusion of zero point vibrational energies. Formation of the complex elongates the OH bond of OOH, whereas the CH bond of CH_3X that participates in the secondary H-bond is shortened. The stretching frequencies associated with these two bonds are shifted to the red and blue, respectively. Complexation is also found to weaken the C−X bond of CH_3X, while strengthening the OO bond of the OOH, as indicated both by bond lengths and by changes in their stretching frequencies. The secondary minimum on the surface contains only CH···O bonds and is held together by roughly 25% of the interaction energy found in the global minimum.

The results are similar in many ways to comparable H-bonds formed between CH_3X and molecules such as HOOH or HCOOH. This degree of similarity suggests that the free radical nature of OOH has only a minor bearing on the fundamental characteristics of the relevant interactions.

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