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G2 Molecular Orbital Investigation of OCH^+-XH, OCH^+-X_2, and $OCH^+-XY(YX)$ ($X = Y = F$, Cl, and Br) Proton Bond Complexes

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The results of theoretical studies on structures and energetics are presented for proton bond complexes OCH^+-XH, OCH^+-X_2, and $OCH^+-XY(YX)$ ($X = Y = F$, Cl, and Br). In all the monocation complexes, the halogen atom shares a proton with CO. The calculated energetic results show that the stability decreases when descending in the corresponding periodic table column. The possible proton transfer dissociation processes of $OCH^+ + XH$, $OCH^+ + X_2$, and $OCH^+ + XY$ systems into XH_2^+, X_2H^+, XYH^+, and YXH^+ and CO are calculated to be exothermic. The natural bond order results show that the largest intermolecular charge transfer is found in the Br bonded complexes.

1. Introduction

Proton bond complexes have long been known as intermediates of proton transfer reactions, which are important in chemical and biological environments. Accurate knowledge of the thermodynamics of complexation energies and dissociative proton transfer reactions would serve as a useful framework from which to build a detailed and quantitative understanding of the nature of the reaction intermediates, reactivity, and mechanism. Numerous experimental and theoretical studies have been devoted to these types of compounds concerning their structural parameters and the nature of reaction intermediates.[1−25] Recently, Radom and Collins reported a systematic theoretical study of the reaction of HF and H_2O with HCO^+. They observed rearrangement, abstraction, exchange, and exchange−rearrangement reactions. They showed that the abstraction reaction is dominant for both the $HF + HOC^+$ and $H_2O + HOC^+$ systems.[26] Sheng and Leszczynski reported about the molecular structures of OCH^+-Rg (Rg = He, Ne, Ar, Kr, Xe) complexes.[27] In this paper, we report our investigation on the OCH^+-HX, OCH^+-X_2, and $OCH^+-XY(YX)$ ($X = Y = F$, Cl, and Br) complexes. The relative stability of these proton bond complexes are examined. The possible proton transfer dissociation processes of $OCH^+ + XH$, $OCH^+ + X_2$, and $OCH^+ + XY$ systems into XH_2^+, X_2H^+, XYH^+, and YXH^+ and molecular CO are also examined. To our knowledge, no comparative ab initio studies of these complexes have been carried out up to now. The electronic structure of these complexes has been analyzed and the relative stabilities are examined.

2. Computational Details

Calculations were performed using the Gaussian 98 program system.[28] The geometry optimizations and frequency calculations were performed at the MP2(full)/6-31G(d) level. Harmonic vibrational frequency calculations were performed to confirm whether the predicted structure is a minimum and to evaluate zero-point vibrational energy (ZPE) corrections. The ZPE corrections were obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[29] Final energies were calculated at the Gaussian-2 (G2)[30] level. The charge distribution in the complexes has been analyzed from the natural bond orbital (NBO)[31] partitioning scheme at the MP2(full)/6-31G(d) level. Atomic populations obtained from this analysis are less basis set dependent than those corresponding to the Mulliken population analysis.[31]

3. Results and Discussion

Association of OCH^+ ($C_{\infty v}$ symmetry) with HX, X_2, and XY leads to C_s symmetry monocation complexes OCH^+-XH, OCH^+-X_2, OCH^+-XY, and OCH^+-YX, which was calculated to be a stable structure at the G2 level of theory. No symmetry constraints were imposed during the optimization process, and the geometry searches were carried out for a number of possible isomers to ensure the location of the global minimum. For the $OCHClF^+$ and $OCHBrF^+$ complexes, the optimization leads to $OCHFCl^+$ and $OCHFBr^+$, respectively. Tables 1, 2, and 3 list the most important optimized geometric parameters of OCH^+-XH, $N_2H^+-X_2$, and OCH^+-XY ($X = Y = F$, Cl, and Br) complexes, respectively, at the MP2(full)/6-31G(d) level of theory. In these tables we also report the calculated association energies of OCH^+ with HX, X_2, and XY. In Table 4, we report the calculated NBO-MP2(full)/6-31G(d) net charge and charge transfer from HX, X_2, and XY moieties to OCH^+. Table 5 lists the G2 calculated thermodynamics values for the proton transfer dissociation process of $OCH^+ + XH$, $OCH^+ + X_2$, and $OCH^+ + XY$ systems into XH_2^+, X_2H^+, XYH^+, and YXH^+ and CO.

In the OCH^+-XH ($X = F$, Cl, and Br) complexes, the halogen atom shares a proton with CO and weakens the H^+-C bond strength. Consequently, the H^+-C bond length becomes

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TABLE 1: MP2(full)/6-31G(d) Optimized Bond Lengths (Å) and Bond Angles (deg) of $OCH^+{-}XH^a$ Complexes and G2 Thermodynamics (kcal/mol) of the Association Process of OCH^+ with XH (X = F, Cl, and Br)

							association process[b]		
complex	C−O	$C{-}H^+$	$H^+{-}X$	X−H	$\angle C{-}H^+{-}X$	$\angle H^+{-}X{-}H$	ΔE_0	ΔH_0	ΔG_{298}
$OCHFH^+$ [c]	1.132	1.138	1.542	0.948	169.61	129.08	−14.40	−15.09	−10.80
	1.133	1.143	1.495	0.934	169.8	129.4			
FH_2^+ [c]			0.967	0.967		113.32			
			0.966	0.966		112.7			
FH				0.922					
$OCHClH^+$	1.132	1.131	2.090	1.287	175.14	109.57	−10.96	−11.54	−7.72
ClH_2^+			1.312	1.312		94.50			
ClH				1.281					
$OCHBrH^+$	1.133	1.146	2.178	1.443	176.34	98.15	−11.87	−12.47	−8.50
BrH_2^+			1.451	1.451		92.53			
BrH				1.423					

[a] The optimized O−C and $C{-}H^+$ bond lengths in OCH^+ ion are respectively 1.136 and 1.112 Å. [b] ΔE_0 is the energy of the association process with zero-point correction (ZPE) and without thermal corrections. [c] The second value corresponds to the MP2/6-31G(d,p) results [from ref 26].

TABLE 2: MP2(full)/6-31G(d) Optimized Bond Lengths (Å) and Bond Angles (deg) of $OCH^+{-}X_2$ Complexes and G2 Thermodynamics (kcal/mol) of the Association Process of OCH^+ with X_2 (X = F, Cl, and Br)

							association process[a]		
complex	C−O	$C{-}H^+$	$H^+{-}X$	X−X	$\angle C{-}H^+{-}X$	$\angle H^+{-}X{-}X$	ΔE_0	ΔH_0	ΔG_{298}
$OCHF_2^+$	1.131	1.109	1.807	1.430	177.05	92.94	−3.46	−3.69	−0.76
F_2H^+			0.987	1.446		104.94			
F2				1.395					
$OCHCl_2^+$	1.132	1.127	2.125	2.022	178.13	99.17	−9.76	−10.01	−6.82
Cl_2H^+			1.314	2.014		99.59			
Cl2				2.010					
$OCHBr_2^+$	1.133	1.121	2.275	2.314	152.01	74.98	−12.84	−13.12	−9.55
Br_2H^+			1.453	2.322		97.58			
Br_2				2.313					

[a] ΔE_0 is the energy of the association process with zero-point correction (ZPE) and without thermal corrections.

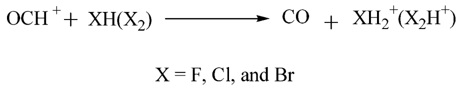
TABLE 3: MP2(full)/6-31G(d) Optimized Bond Lengths (Å) and Bond Angles (deg) of $OCH^+{-}XY(YX)$ Complexes and G2 Thermodynamics (kcal/mol) of the Association Process of OCH^+ with XY (X = Y = F, Cl, and Br)

							association process[a]		
complex	C−O	$C{-}H^+$	$H^+{-}X(Y)$	X−Y	$\angle C{-}H^+{-}X$ or $\angle C{-}H^+{-}Y$	$\angle H^+{-}X{-}Y$ or $\angle H^+{-}Y{-}X$	ΔE_0	ΔH_0	ΔG_{298}
$OCHFCl^+$	1.132	1.133	1.590	1.689	170.16	118.07	−10.52	−10.86	−6.76
$ClFH^+$			0.963	1.784		111.63			
FCl				1.642					
$OCHFBr^+$	1.132	1.147	1.516	1.824	170.67	119.05	−14.79	−15.17	−10.72
$BrFH^+$			0.955	1.951		114.10			
BrF				1.778					
$OCHClBr^+$	1.132	1.116	2.161	2.175	158.52	78.60	−11.82	−12.03	−8.47
$BrClH^+$			1.456	2.145		97.44			
BrCl				2.163					
$OCHBrCl^+$	1.132	1.137	2.214	2.165	174.35	89.34	−10.68	−10.96	−7.20
$ClBrH^+$			1.310	2.199		99.59			

[a] ΔE_0 is the energy of the association process with zero-point correction (ZPE) and without thermal corrections.

longer than in the isolated OCH^+ ion. Indeed, the MP2(full)/6-31G(d) level calculated $H^+{-}C$ distance in the free OCH^+ ion is about 1.04 Å. The calculated $H^+{-}C$ bond lengths are elongated to 1.138, 1.131, and 1.146 Å in the $OCH^+{-}FH$, $OCH^+{-}ClH$, and $OCH^+{-}BrH$ complexes, respectively. The calculated $H^+{-}X$ bond lengths are 1.542, 2.090, and 2.178 Å, respectively for X = F, Cl, and Br. On the other hand, we noticed that the association of OCH^+ with XH does not affect the O−C and X−H distances significantly (Table 1): the O−C distance becomes only slightly shorter from 1.136 to 1.132 Å and the X−H distance becomes longer by 0.026, 0.006, and 0.02 Å, respectively for X = F, Cl, and Br. In addition, for the $OCH^+{-}FH$ complex, our results are in good agreement with recently reported values (Table 1).[26] These observations indicate that the $OCH^+{-}XH$ (X = F, Cl, and Br) complexes are of proton bond complex types. Indeed, the respectively complexation energies are −14.40, −10.96, and −11.87 kcal/mol. However, the complexation energy decreases when descending in the corresponding periodic table column. The same trends are observed at room temperature (298 K).

SCHEME 1



On the other hand, the structure of $OCH^+{-}XH$ (X = Cl and Br) can be viewed as a weak complex between XH_2^+ and molecular CO. Thus, the dissociative proton transfer processes of OCH^+ + XH into XH_2^+ and CO (Scheme 1) are exothermic by about −27, −9, and −3 kcal/mol for OCH^+ + FH, OCH^+ + ClH, and OCH^+ + BrH systems, respectively (Table 5). At room temperature (298 K) the dissociative proton transfer processes are also exothermic for OCH^+ + FH and OCH^+ + ClH systems and slightly endothermic for the OCH^+ + BrH system. Indeed, for the $OCH^+{-}BrH$ complex, the structure

TABLE 4: NBO-MP2(full)/6-31G(d) Net Charge (electron) and Charge Transfer Q_t (electron) from Isolated XH, X_2, and XY to OCH^+

complex	$q(H_{end})$	$q(X)$	$q(Y_{end})$	Q_t
FH	0.55	−0.55		
ClH	0.28	−0.28		
BrH	0.22	−0.22		
FCl		−0.32	0.32	
FBr		−0.38	0.38	
ClBr		−0.08	0.08	
$OCHFH^+$	0.62	−0.53		0.08
$OCHClH^+$	0.34	−0.23		0.10
$OCHBrH^+$	0.27	−0.13		0.14
$OCHF_2^+$		0.01	0.04	0.05
$OCHCl_2^+$		0.02	0.08	0.10
$OCHBr_2^+$		0.08	0.05	0.13
$OCHFCl^+$		0.43	−0.35	0.08
$OCHFBr^+$		−0.41	0.51	0.10
OCHClBr		−0.03	0.13	0.11
$OCHBrCl^+$		0.14	−0.01	0.13

TABLE 5: G2 Thermodynamics (kcal/mol) of the Dissociative Proton Transfer Processes

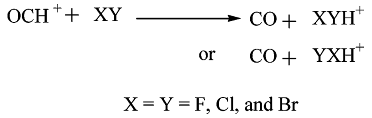
	ΔE_0	ΔH_0	ΔG_{298}
$OCH^+ + FH \rightarrow FH_2^+ + CO$	−27.31	−27.30	−23.80
$OCH^+ + ClH \rightarrow ClH_2^+ + CO$	−8.80	−8.78	−5.12
$OCH^+ + BrH \rightarrow BrH_2^+ + CO$	−3.20	−3.19	+0.54
$OCH^+ + F_2 \rightarrow F_2H^+ + CO$	−56.75	−56.76	−52.60
$OCH^+ + Cl_2 \rightarrow Cl_2H^+ + CO$	−10.89	−10.93	−6.58
$OCH^+ + Br_2 \rightarrow Br_2H^+ + CO$	−1.40	−1.47	+2.98
$OCH^+ + FCl \rightarrow FClH^+ + CO$	−22.67	−22.67	−18.82
$OCH^+ + FCl \rightarrow ClFH^+ + CO$	−28.23	−28.31	−24.44
$OCH^+ + FBr \rightarrow FBrH^+ + CO$	−15.68	−15.69	−11.77
$OCH^+ + FBr \rightarrow BrFH^+ + CO$	−15.15	−15.35	−11.38
$OCH^+ + ClBr \rightarrow ClBrH^+ + CO$	−6.03	−6.07	−2.10
$OCH^+ + ClBr \rightarrow BrClH^+ + CO$	−4.83	−4.91	−0.90

can be viewed as a weak complex between OCH^+ and BrH rather than BrH_2^+ and CO. These tendencies are in good agreement with the $C-H^+$ bond distance, which is closer to the $C-H^+$ distance in free OCH^+ fragment for OCH^+-BrH complex and longer for OCH^+-FH and OCH^+-ClH complexes (Table 1).

In addition, from the NBO results, we can see that the charge transfer from XH fragment to OCH^+ ion is more important in OCH^+-ClH and OCH^+-BrH complexes than in the OCH^+-FH one (see Table 4). We can also see that the largest intermolecular charge transfer comes from an X atom rather than a hydrogen atom. Upon complexation, there is a net flow of electrons from the X atom to the cation.

In the OCH^+-X_2 (X = F, Cl, and Br) dihalogen and $OCH^+-XY(YX)$ (X = Y = F, Cl, and Br) interhalogen complexes, the halogen atom also shares a proton with CO and weakens the H^+-C bond strength. The H^+-C bond length becomes longer than in the isolated OCH^+ ion (see Tables 2 and 3). On the other hand, we noticed that the association of OCH^+ with X_2 and XY does not affect the O−C, X−X, and X−Y distances significantly: the O−C distance becomes slightly longer, the X−X distance becomes longer, and the X−Y distance becomes shorter when the more polarizable atom is bonded and slightly longer when the less polarizable atom is bonded. These observations indicate that the OCH^+-X_2, OCH^+-XY, and OCH^+-YX complexes are of proton bond complex types. Indeed, the complexation energies are −3.46, −9.76, and −12.84 kcal/mol, respectively for OCH^+-F_2, OCH^+-Cl_2, and OCH^+-Br_2. For the OCH^+-XY, and OCH^+-YX complexes the complexation energy is in the range −10 to − 15 kcal/mol. The same trends are observed at room temperature (298 K). On the other hand, we noticed that the calculated H^+-X bond lengths are longer in complex than in free protonated dihalogens X_2H^+ and interhalogens YXH^+ and XYH^+. Nevertheless, the structure of OCH^+-X_2, OCH^+-XY, and OCH^+-YX (X = F, Cl, and Br) complexes can also be viewed as a weak complex between X_2H^+, YXH^+, and XYH^+ and CO. Thus, the dissociative proton transfer processes of $OCH^+ + X_2$ into X_2H^+ and CO (Scheme 2) are exothermic by about 57, 11, and 2 kcal/mol for $OCH^+ + F_2$, $OCH^+ + Cl_2$, and $OCH^+ + Br_2$, respectively (Table 5). The dissociative proton transfer processes of $OCH^+ + XY(YX)$ into $XY(YX)H^+$ and CO (Scheme 2) are endothermic (Table 5). The same trends are observed at room temperature (298 K), except for the $OCH^+ + Br_2$ system. These results indicate that we cannot observe a direct dissociative proton transfer process of $COH^+ + Br_2$ into Br_2H^+ and CO.

SCHEME 2



On the other hand, from the NBO results, we can see that the intermolecular charge transfer from X_2 and XY fragments to OCH^+ ion is found to be more important in the bromine-bonded complexes (see Table 4). We can also see that the most important transferred charge comes from bonding to H ($X(H^+)$) atom rather than the $X(Y)_{end}$ one. Upon complexation, there is a net flow of electrons from the $X(H^+)$ atom to the cation, resulting in a more positive atomic charge on $X(H^+)$ rather than on $X(Y)_{end}$ ones.

4. Conclusion

Complexes of OCH^+ with XH, X_2, and XY (X = Y = F, Cl, and Br) were found to have C_s symmetry with a halogen atom sharing a proton with CO. Formation of ions OCH^+-XH, OCH^+-X_2, and $OCH^+-XY(YX)$ (X = F, Cl, and Br) were calculated to be exothermic by 4−15 kcal/mol at the G2 level of theory. The calculated energetic results show that the stability of the ions depends on the type of the halogen bonded to OCH^+. The possible proton transfer dissociation processes of $OCH^+ + XH$, $OCH^+ + X_2$, and $OCH^+ + XY$ complexes into XH_2^+, X_2H^+, XYH^+, and YXH^+ and CO are calculated to be exothermic. The NBO results show that the largest intermolecular charge transfer is found in the Br-bonded complexes. These observations indicate that the OCH^+-XH, OCH^+-X_2, and $OCH^+-XY(YX)$ complexes should be experimentally observable in the gas phase.

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