Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Mass Spectrometry 240 (2005) 1–5
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Ab initio molecular orbital investigation of $SiOH^+$–XH, $SiOH^+$–X_2 and $SiOH^+$–XY(YX) (X = Y = F, Cl and Br) proton-bond complexes

Mohammad Solimannejad[a,*], Masoud Haratian[a], Abderrahim Boutalib[b]

[a] *Quantum Chemistry Group, Department of Chemistry, Arak University, 38156-879 Arak, Iran*
[b] *Département de Chimie, Université Cadi Ayyad, Faculté des Sciences Semlalia, B.P. 2390 Marrakech, Morocco*

Received 31 July 2004; accepted 5 October 2004
Available online 11 November 2004

Abstract

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

Keywords: Proton-bond complexes; Ab initio; NBO; Charge transfer; Stability

1. Introduction

Proton-bond complexes are long been known as intermediates of proton transfer reactions, which are important in physical, chemical and biological properties and processes. Accurate knowledge of the thermodynamics, reactivity and mechanism of complexation and dissociative proton transfer reactions would serve as a useful framework. Numerous experimental and theoretical studies have been devoted to this type of compounds concerning their structural parameters, the nature of the reaction intermediates [1–21]. On the other hand, Bohme and co-workers have extensively studied the gas-phase reactions of Si^+ and $SiOH^+$ with small molecules. They provide insight of the chemical bonding of silicon with hydrogen, carbon, nitrogen, oxygen and sulfur [22–25]. Recently, Dopfer and co-workers have reported about the infrared photodissociation spectra and molecular structures of $SiOH^+$–X (X = He, Ne, Ar, N_2) and $SiOH^+$–Ar_n (n = 1–10) ionic hydrogen complexes [26,27]. They have showed that experimentally and theoretically, all studied complexes prefer linear configurations. More recently we reported theoretical studies on structures and energetics for proton-bond complexes N_2H^+–XH, N_2H^+–X_2 and N_2H^+–XY(YX) (X = Y = F, Cl and Br) at the B3LYP/6-311++G(3df,3pd) level of theory [28]. We have shown that in all the monocations complexes, the halogen atom shares a proton with N_2. We have also shown that the stability decreases when descending in the corresponding periodic table column and the possible proton transfer dissociation processes of $N_2H^+ + XH$, $N_2H^+ + X_2$ and $N_2H^+ + XY$ systems into XH_2^+, X_2H^+, XYH^+ and YXH^+ and molecular N_2 are endothermic. In this paper, we report our investigation on the $SiOH^+$–HX, $SiOH^+$–X_2 and $SiOH^+$–XY(YX) (X = Y = F, Cl and Br) complexes. The possible proton transfer dissociation processes of $SiOH^+ + XH$, $SiOH^+ + X_2$ and $SiOH^+ + XY$ systems into XH_2^+, X_2H^+, XYH^+ and YXH^+, and SiO are examined. To our knowledge, no comparative ab initio studies of these complexes have been carried out up to

* Corresponding author. Tel.: +98 861 2777401; fax: +98 861 2774031.
E-mail address: m-solimannejad@araku.ac.ir (M. Solimannejad).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.10.002

now. The electronic structure of these complexes has been analyzed and the relative stabilities are examined.

2. Computational details

Calculations were performed using the GAUSSIAN98 program system [29]. The geometry optimizations and frequency calculations were performed at the MP2(full)/6-31++G(d,p) level. Harmonic vibrational frequency calculations were performed to confirm whether the predicted structure is a minimum and to evaluate zero-point vibrational energies (ZPE) corrections. The ZPE corrections are obtained from scaled MP2(full)/6-31++G(d,p) frequencies (scaled by the factor 0.96) [30]. Final energies were calculated at the QCISD(T)/6-31++G(d,p)//MP2(full)/6-31++G(d,p) + ZPE level. The charge distribution in the complexes has been analyzed from the natural bond orbital (NBO) [31] partitioning scheme at the MP2(full)/6-31++G(d,p) level. Atomic populations obtained from this analysis are fewer bases set dependent than those corresponding to the Mulliken population analysis [31].

3. Results and discussion

Association of $SiOH^+$ ($C_{\infty v}$ symmetry) with HX, X_2 and XY leads to C_s symmetry monocation complexes $SiOH^+$–XH, $SiOH^+$–X_2, $SiOH^+$–XY and $SiOH^+$–YX that was calculated to be a stable structure at the MP2(full)/6-31++G(d,p) 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 association of $SiOH^+$ with FH, we have found two stable conformations: the conformation where the halogen atom shares a proton with SiO and the HF–$SiOH^+$ conformation where the halogen atom is bonded to Si atom. The $SiOH^+$–FH conformation is the more stable at the QCISD(T)/6-31++G(d,p)//MP2(full)/6-31++G(d,p) + ZPE level. For the $SiOH^+$–ClF and $SiOH^+$–BrF complexes, the optimization leads to $SiOH^+$–FCl and $SiOH^+$–FBr, respectively. Tables 1–3 list the most important optimized geometrical parameters of $SiOH^+$–XH, $SiOH^+$–X_2 and $SiOH^+$–XY(YX) (X = Y = F, Cl and Br) complexes, respectively. Tables 4 and 5 list the MP2(full)/6-31++G(d,p) unscaled vibrational frequencies of all investigated complexes along with the corresponding $SiOH^+$ monomer values. In Table 6 we reported the calculated association energies of $SiOH^+$ with HX, X_2 and XY(YX). We also reported in Table 6 the calculated NBO–MP2(full)/6-31++G(d,p) charge transfer from HX, X_2 and XY(YX) moieties to $SiOH^+$. Table 7 lists the energy for the proton transfer dissociation process of $SiOH^+$ + XH, $SiOH^+$ + X_2 and $SiOH^+$ + XY(YX) systems into XH_2^+, X_2H^+, XYH^+ and YXH^+, and SiO.

Table 1
MP2(full)/6-31++G(d,p) optimized bond lengths (Å) and bond angles (°) of $SiOH^+$–XH complexes (X = F, Cl and Br)[a]

Compound	Si–O	O–H^+	H^+–X	X–H	∠H^+–X–H
$SiOHFH^+$	1.554	0.991	1.576	0.935	135.2
FH_2^+			0.969	0.969	113.2
FH				0.926	
$SiOHClH^+$	1.556	0.996	2.006	1.275	106.2
ClH_2^+			1.293	1.293	95.7
ClH				1.281	
$SiOHBrH^+$	1.555	1.005	2.074	1.440	98.5
BrH_2^+			1.430	1.430	93.2
BrH				1.406	

[a] The optimized O–Si and O–H^+ in $SiOH^+$ ion are 1.574 and 0.98 Å, respectively.

Table 2
MP2(full)/6-31++G(d,p) optimized bond lengths (Å) and bond Angles (°) of $SiOH^+$–X_2 complexes (X = F, Cl and Br)

Compound	Si–O	O–H^+	H^+–X	X–X	∠H^+–X–X
$SiOHF_2^+$	1.558	0.986	1.810	1.437	98.6
F_2H^+			0.999	1.440	100.9
F2				1.433	
$SiOHCl_2^+$	1.557	0.992	2.030	2.023	99.6
Cl_2H^+			1.298	2.032	99.6
Cl_2				2.019	
$SiOHBr_2^+$	1.555	1.002	2.087	2.313	91.2
Br_2H^+			1.433	2.315	96.6
Br_2				2.313	

In the $SiOH^+$–XH (X = F, Cl and Br) complexes, the halogen atom shares a proton with SiO and weakens the H^+–O bond strength. Consequently, the H^+–O bond length becomes longer than in the isolated $SiOH^+$ ion. Indeed, the MP2(full)/6-31++G(d,p)-level-calculated H^+–O distance in the free $SiOH^+$ ion is 0.975 Å. The calculated H^+–O bond lengths are elongates to 0.991, 0.996 and 1.005 Å in the $SiOH^+$–FH, $SiOH^+$–ClH and $SiOH^+$–BrH complexes, respectively. Thus the lengthening of the H^+–O bond is the major effects of complexation on the $SiOH^+$ properties and

Table 3
MP2(full)/6-31++G(d,p) optimized bond lengths (Å) and bond angles (°) of $SiOH^+$–XY(YX) complexes (X = Y = F, Cl and Br)

Compound	Si–O	O–H^+	H^+–X (Y)	X–Y	∠H^+–X–Y or ∠H^+–Y–X
$SiOHFCl^+$	1.556	0.990	1.597	1.691	123.7
$ClFH^+$			0.968	1.787	112.2
FCl				1.667	
$SiOHFBr^+$	1.555	0.995	1.547	1.821	133.2
$BrFH^+$			0.962	1.941	114.1
BrF				1.793	
$SiOHClBr^+$	1.556	0.995	2.000	2.175	97.1
$BrClH^+$			1.295	2.202	98.3
BrCl				2.163	
$SiOHBrCl^+$	1.556	1.000	2.095	2.163	93.4
$ClBrH^+$			1.434	2.150	97.0