Contents lists available at ScienceDirect

Chemical Physics Letters

Research paper

Proton affinities of hydrated molecules

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ARTICLE INFO

ABSTRACT

Proton affinities (PA) of non-hydrated, M, and hydrated forms, $M(H_2O)_{1,2,3}$, of 20 organic molecules including alcohols, ethers, aldehydes, ketones and amines were calculated by the B3LYP/6-311++G(d,p) method. For homogeneous families, linear correlations were observed between PAs of the $M(H_2O)_{1,2,3}$ and the PAs of the non-hydrated molecules. Also, the absolute values of the hydration enthalpies of the protonated molecules decreased linearly with the PAs. The correlation functions predicted that for an amine with PA < 1100 kJ/mol the PA(M(H_2O)) is larger than the corresponding PA, while for an amine with PA > 1100 kJ/mol the PA(M(H_2O)) is smaller than the PA.

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1. Introduction

Proton transfer is an important reaction in biological, chemical and atmospheric systems [1,2]. Proton affinity (PA), which is defined as $-\Delta H$ of protonation reaction in gas phase, is a key parameter in the study of the systems including proton transfer reactions. Therefore, considerable efforts have been made to determine the PAs of different molecules using experimental techniques and computational methods [3–7]. Mass spectrometric (MS) techniques such as time of flight-MS [8], ion trap-MS [9] and ion mobility spectrometry [5,6] have been employed to study the proton transfer reactions and measure the PAs of various types of compounds.

Although neutral (M) and protonated molecules (MH+) present as isolated or bare species in high vacuum condition and in the absence of protic molecules such as H_2O, they are hydrated in ambient condition [10,11]. Therefore, effect of hydration on the thermochemistry of protonation and PA values is an important factor. Hydration energies of neutral and protonated molecules have been obtained for numerous molecules using experimental and computational methods [12,13]. It has been reported that the hydration energies for the molecules with higher PAs are larger [14]. The hydration can change the mechanism and kinetics of ion-molecule reactions. Hydration slows down the rate of proton-bound dimer formation [15] while it catalyzes the intramolecular proton transfer reactions (tautomerisms) [16].

In this work, PAs of mono-, di- and tri-hydrated forms of 20 organic molecules are calculated and some correlations between them and the enthalpies of the hydrations are obtained.

2. Computational details

The structures of the non-hydrated, hydrated, and protonated molecules were fully optimized employing DFT method using the B3LYP functional. The 6-311++G(d,p) basis set was used for all calculations which includes enough polarization and diffusion functions. It has been reported that the DFT method with large basis sets gives reliable structural and energetic properties for systems with hydrogen bonding interactions [17]. Furthermore, to benchmark the method, the calculated proton affinities (PA) of the molecules were compared with the corresponding experimental data. Frequency calculations were performed at the same level of theory to obtain the enthalpies (ΔH) of the processes. All calculations were performed using Gaussian 09 software [18].

3. Results and discussion

There are two paths for formation of hydrated protonated molecules, $MH^+(H_2O)_n$: Hydration of protonated molecules and protonation of hydrated molecules. In this work, we study mono-, di-and tri-hydrated systems. Fig. 1 shows schematically the different paths for formation of hydrated protonated molecules; the enthalpy of each path has been shown on the arrow of the reaction. The -PAs are the enthalpies of the protonation reactions, ΔH_{1-M} is the enthalpy of mono-hydration of the neutral

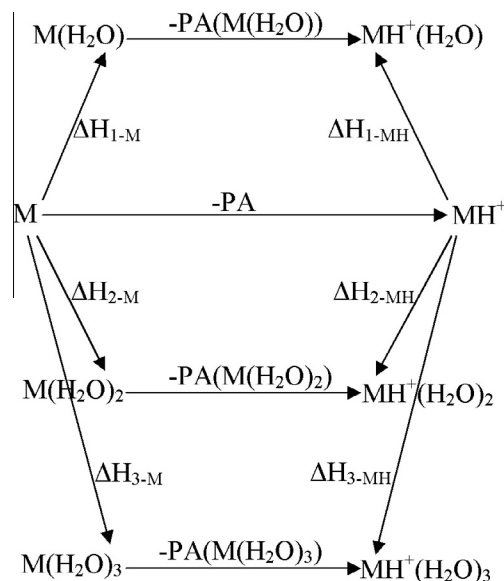E-mail address: y.valadbeigi@ch.iut.ac.ir

Fig. 1. Schematic presentation of the different paths for hydration of a protonated molecule and protonation of a hydrated molecule as well as enthalpies of the paths.

molecule, and $\Delta H_{1\text{-MH}}$ is the enthalpy of mono-hydration of the protonated molecule. The $\Delta H_{2\text{-M}}$, $\Delta H_{3\text{-M}}$, $\Delta H_{2\text{-MH}}$ and $\Delta H_{3\text{-MH}}$ are defined as the same way.

According to Hess' law, the enthalpies of the two paths for formation $MH^+(H_2O)_{1,2,3}$ are the same. Therefore, the enthalpies of hydrations and the PAs may have some relationships. The aim of this work is to explore effect of hydration on the PAs of molecules and find some correlations between the PAs and the ΔH values. Therefore, hydrations and protonations of 20 organic molecules with different function groups were investigated. The optimized structures of the mono-, di- and tri-hydrated forms of these molecules have been shown in Supplementary Materials (Fig. S1). Some of these molecules such as methanol may be hydrated from two different paths: hydrogen bond formation between the hydrogen atom of methanol and the oxygen atom of water, or hydrogen bond formation between the oxygen atom of methanol and one of the hydrogen atoms of water. However, only the most stable structures were considered in this work.

Fig. 2 shows the optimized structures of the mono-, di- and tri-hydrated forms of the protonated molecules. The numbers on the bonds are the hydrogen bond distances in angstrom. The complete geometrical parameters (bond lengths, angles and dihedrals) of the all hydrated and protonated molecules have been collected in Supplementary Materials (Figs. S2 and S3).

The calculated enthalpies of hydrations of the neutral and protonated molecules have been summarized in Table 1. Also, the calculated PA values for the isolated and hydrated molecules have been tabulated in Table 2. The enthalpies of mono-hydration ($\Delta H_{1\text{-M}}$) for alcohols are approximately the same (about −18 kJ/mol). Formaldehyde has the minimum values of $\Delta H_{1\text{-M}}$ and PA while the amines have the maximum values of $\Delta H_{1\text{-M}}$ and PA. The $\Delta H_{1\text{-M}}$ values indicate the strength of the hydrogen bonding interactions between hydrogen atom of H_2O and oxygen or nitrogen atoms of the organic molecules. The enthalpies of di-hydrations ($\Delta H_{2\text{-M}}$) are more than twice of the corresponding $\Delta H_{1\text{-M}}$ values because there is an additional hydrogen bond between oxygen atom of H_2O and hydrogen atoms of the alkyl groups of the molecules (See Fig. S1).

Table 1 shows that the absolute values of the enthalpy of hydrations of the protonated molecules ($\Delta H_{1\text{-MH}}$, $\Delta H_{2\text{-MH}}$ and $\Delta H_{3\text{-MH}}$) are larger than those for isolated molecules ($\Delta H_{1\text{-M}}$, $\Delta H_{2\text{-M}}$ and $\Delta H_{3\text{-M}}$). Because the hydration of the protonated molecules, MH^+, proceeds via the strong ion-molecule interaction while the weaker hydrogen bonding interaction is responsible for the hydration of the neutral molecules. As the PA increases the $|\Delta H_{1\text{-MH}}|$, $|\Delta H_{2\text{-MH}}|$ and $|\Delta H_{3\text{-MH}}|$ decrease, i.e. for a molecule, M, with higher PA, the tendency of MH^+ for hydration is low. Fig. 3a –c shows the correlations between the $\Delta H_{1,2,3\text{-MH}}$ values and the PAs. Linear relationships are observed for the $\Delta H_{1\text{-MH}} - PA$, $\Delta H_{2\text{-MH}} - PA$ and $\Delta H_{3\text{-MH}} - PA$ data of homogeneous families (alcohols & ethers, aldehydes & ketones and amines). The R-squared (R^2) values have been shown for the correlation functions. The R^2 values are generally more than 0.9. In the case of the protonation of the stronger bases (with higher PAs), the positive charge of the proton is distributed throughout the protonated molecule, and the remained positive charge on the H atom of the MH^+ is small [19]; therefore, its interaction with oxygen atom of H_2O is a hydrogen bonding interaction rather than a strong ion-molecule interaction. On the other hand, when a weak base (with lower PA) is protonated, the most portion of the positive charge remains on the hydrogen atom; therefore, a strong interaction is established between the H atom of the MH^+ and the oxygen of the water molecule. In general, the absolute values of $\Delta H_{1\text{-M}}$, $\Delta H_{2\text{-M}}$ and $\Delta H_{3\text{-M}}$, increase non-linearly with PA (Fig. S4 in Supplementary Materials) and the absolute values of the $\Delta H_{1\text{-MH}}$, $\Delta H_{2\text{-MH}}$ and $\Delta H_{2\text{-MH}}$ decrease linearly as PA increases.

Fig. 3d–f shows correlations between the proton affinities of the isolated and hydrated molecules. The PAs of the hydrated molecules, $PA(M(H_2O)_{1,2,3})$, are linear functions of the PAs of the isolated molecules. Excellent linear correlations were observed for homogeneous families. The R^2 values indicate that the correlations are satisfactory linear except for the tri-hydrated alcohols. The slopes of the $PA(M(H_2O)_{1,2,3})-PA$ for amines are larger than those for alcohols, ethers, aldehydes and ketones. Furthermore, as the hydration amount increases the slopes of the graphs in Fig. 3d–f decrease. In the case of the amines, for example, the slopes are 0.71, 0.68 and 0.48 in Fig. 3d–f, respectively. Although for the studied molecules the $PA(M(H_2O)_{1,2,3})$ values are larger than the corresponding PAs, the correlation functions of Fig. 3d–f predict that for an amine with PA > 1100 kJ/mol, a ketone with PA > 1020 kJ/mol and an ether with PA > 980 kJ/mol the $PA(M(H_2O)_{1,2,3})$ values become smaller than the corresponding PAs. Since the PAs of ethers and ketones are generally smaller than 1000 kJ/mol, the $PA(M(H_2O)_{1,2,3}) < PA$ is possible only for amines. According to Hess' law we have

$$|\Delta H_{1\text{-MH}}| + PA = |\Delta H_{1\text{-M}}| + PA\,(M(H_2O)) \tag{1}$$

Since the $|\Delta H_{1\text{-MH}}|$ decreases while the $|\Delta H_{1\text{-M}}|$ increases as the PA increases, the following equation may be established for a special PA: $\Delta H_{1\text{-MH}} = \Delta H_{1\text{-M}}$, and consequently, $PA = PA\,(M(H_2O))$. If $|\Delta H_{1\text{-MH}}| > |\Delta H_{1\text{-M}}|$, we have $PA < PA\,(M(H_2O))$ and for $|\Delta H_{1\text{-MH}}| < |\Delta H_{1\text{-M}}|$, we have $PA > PA\,(M(H_2O))$. These results demonstrate that the enthalpies of the hydration of the neutral and protonated molecules and proton affinities of the hydrated molecules can be determined from the PAs.

Fig. 4 shows the effect of number of the hydrating water molecules on the proton affinities of the hydrated molecules. The effect of the first water molecule on the PAs of the mono-hydrated molecules is more than that for the second or third water molecule. In the case of methanol, for example, as the first, second and third