# *Ab initio* and density functional theory calculations of proton affinities for volatile organic compounds

T. Wróblewski[1], L. Ziemczonek[1], A.M. Alhasan[1], and G.P. Karwasz[2]

[1]Institute of Physics, Pomeranian Academy, 76-200 Słupsk, Poland
[2]Institute of Physics, Nicolaus Copernicus University, 87-100 Toruń, Poland

**Abstract.** The Hatree-Fock method with 6-311G** split-valence molecular orbitals basis sets and the density function theory-B3LYP have been applied to geometrical optimizations and calculations of total electronic, zero point vibrational energies and proton affinities at 298 K for volatile organic compounds. Calculated values of proton affinities are compared with experimental data.

## 1 Introduction

Protonation reactions play an important role in organic chemistry and biochemistry [1–3] and are the first steps in many fundamental chemical rearrangements, for example in ion-neutral interactions in gaseous plasma environments [4]. Two quantities are used to characterize the capability of an atom or molecule in the gas phase to accept a proton. Basicity is the negative of the free energy change associated with the reaction. But the most frequently used parameter is the proton affinity (PA) defined as the negative of the enthalpy change of a protonation reaction at standard conditions.

Dynamics of proton transfer is also important for ionization processes in mass spectroscopy. Usually, collisional ionization processes, for example by electron impact, lead to molecule fragmentation. These ionized fragments make difficult the analysis of mass spectra, in particular in the case of volatile organic compounds with their quite complicated structural forms. Proton transfer reaction mass spectrometry (PTR MS) using the hydronium ion ($H_3O^+$) as the ionizing factor allows to avoid these problems [5].

Experimental determination of proton affinities of molecules is not easy [6]. Relative values of PA are most often determined by mass spectroscopic measurement of the equilibrium constant for the proton-exchange gas phase reaction $MH^+ + B \leftrightarrow M + BH^+$ [7,8]. Absolute proton affinities can be obtained from ionization thresholds for the $MH \leftrightarrow MH^+ + e^-$ reaction [8] but not in all cases these MH molecules exist. For this reason, in recent years much attention has been given to the possibility of calculating proton affinities by quantum methods [9–13]. Though *ab initio* methods are very successful in providing reliable values of proton affinities and gas phase basicities for small molecules but still impractical for larger molecules. Semiempirical methods such as AM1, MNDO and PM3, are not consistently reliable in calculations of proton affinities as shown in work [14]. The Density Functional Theory (DFT) has gained a great deal of popularity as a tool for quantum chemistry in the last ten years. In this work we present

the comparison between *ab initio* and DFT calculations of proton affinities for selected small organic systems (hydrocarbons, alcohols, aldehydes, esters) at 298 K.

## 2  Method

Proton affinities, defined as the negative enthalpy change at 298 K for the reaction $A + H^+ \rightarrow AH^+$, have been calculated according to the following expression [15]:

$$PA = \Delta E_{el} + \Delta ZPVE + \Delta E_{vib}(T) + 5/2RT.$$

$\Delta E_{el}$, $\Delta ZPVE$, $\Delta E_{vib}$ are the differences between the total electronic energy, the zero point vibrational and the temperature-dependent portion of vibrational energy of the base molecule and its protonated form at 298 K, respectively. The $5/2RT$ value corresponds to changes of thermal translational and rotational energies of reactants and products at 298 K and 0 K. The temperature dependent portion of vibrational energies is calculated from formula:

$$\Delta E_{vib}(T) = \sum_{i=1}^{3n-6} \frac{Nhv_i}{e^{Nhv_i/RT} - 1},$$

where $n$ denotes the number of atoms in the molecule, $N$ is the Avogadro's number, $v_i$ are the calculated vibrational frequencies.

The Restricted Hatree-Fock method with 6-311G** split-valence molecular orbitals basis sets [16] with two polarization functions has been applied to geometrical optimizations and calculations of total and zero point and termal vibrational energies for neutral and protonated organic species. We have also calculated these energies in density functional theory, using single point calculations of Becke's three parameter hybrid method employing the Lee, Yang and Parr correction function (B3LYP) [17] in conjunction with the split valence polarized basis set 6-311G**.

## 3 Results and discussion

For hydrocarbons we have performed the geometrical optimization for several different molecular configurations. Total energies of methane and ethane are minimal for configurations in which the extra proton is attached to one of the hydrogen atoms and for other molecules - in which the extra proton is attached to one of the border carbon atoms.

Proton affinities compared to experimental data [18,19] are shown in Table 1. Generally, the calculated *ab initio* $PA$ values for alkanes increase with number of C atoms. This increase amounts from 124.9 kcal/mol for methane to 161.75 kcal/mol for hexane if calculated in the HF method and from 127.1 kcal/mol to 159.3 kcal/mol in DFT method for the two molecules, respectively. $PA$ values for alkenes (and alkynes) are higher than for alkanes; this is obvious as the extra proton can in some way substitute lacking hydrogen atoms in non-saturated hydrocarbons. Generally the HF/6-311G** values for all presented hydrocarbons agree well with experimental data (for example disagreements are about 5.8% for ethane and 6.1% for isobutane). For DFT calculations agreements with experimental data are better−disagreements are about 4.7% and 3.3% for ethane and isobutane. The best agreement is for propane–the difference for both methods is below 0.1%. There are no experimental data of PA for butane, pentane and hexane.

**Table 1.** Comparison of calculated proton affinities in Hartee-Fock (HF) and Density Functional Theory (B3-LYP) of small hydrocarbons with experimental results.

| Substance | Formula | PA (kcal/mol) | | |
|-----------|---------|----------------------|-----------------|------------------|
| | | Experiment[a] | Theory | |
| | | | HF/6-311G** | B3-LYP/6-311G** |
| Methane | $CH_4$ | 129.9 | 124.90 | 127.06 |
| Ethene | $C_2H_4$ | 162.6 | 167.61 | 158.78 |
| Ethane | $C_2H_6$ | 142.5 | 134.15 | 135.82 |
| Propyne | $C_3H_4$ | 178.8 | 181.59 | 183.97 |
| Propene | $C_3H_6$ | 179.6 | 186.71 | 163.19 |
| Propane | $C_3H_8$ | 149.5 | 152.18 | 149.60 |
| Butane | $C_4H_{10}$ | | 157.56 | 158.54 |
| Isobutane | $C_4H_{10}$ | 162.0 | 171.92 | 167.32 |
| Pentane | $C_5H_{12}$ | | 158.32 | 158.59 |
| Hexane | $C_6H_{14}$ | | 161.75 | 159.32 |

[a]$PA$ was taken from NIST data compilations [19], see references therein.

Note that our earlier calculations of geometrical configurations [20] showed that the bond between C atom with a proton added and its nearest neighbour is subject to a considerable elongation and the total positive charge transfers to the other part of molecule, i.e. the $CH_4$ molecule separates from the new formed $C_{n-1}H_n^+$ ion. This effect can be expressed by the following reaction scheme:

$$H^+C_nH_{2n+2} = C_{n-1}H_n^+ + CH_4.$$
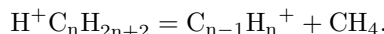
For example, these bond lengths rise up to 3.6 Å and 3.8 Å for protonated ethane and hexane, respectively and it is possible that $H^+C_nH_{2n+4}$ ions are unstable. Also the calculated enthalpies for these reactions are small (5.11 kcal/mol for ethane and only 0.34 kcal/mol for hexane) and show that in room temperature protonated alkanes can undergo decomposition with detachment of $CH_4$.

For oxygenated VOCs, we assumed that the extra proton is attached to the oxygen atom. Some of these molecules include two oxygen atoms and two stable geometrical configurations are possible for them. For example, the differences in $PA$ values caclulated in HF method for the two configurations for $H^+CH_3COOH$, $H^+CH_3COOCH_3$ and $H^+CH_3COOC_2H_5$ are as higher as 13.90, 26.70 and 19.56 kcal/mol, respectively. The lower energetically configuration is that in which an extra proton is attached to the non-hydroxyl oxygen atom (i.e. that which traditionally showed as bound by the double C=O bond). Ion this sense the extra proton leads to some more symmetric structure; in the case of acetic acid one can consider forming of two, almost equivalent O-H groups attached to the carboxylic C atom.

Present $PA$ values in HF and DFT method are compared with experimental ones in table 2 (if more than one configuration is possible, we give the lowest one). The agreement between our calculations and experimental $PA$ for oxygenated VOCs is even better than for hydrocarbons. Similarly to the case of hydrocarbons, the DFT method gives better agreements than the HF *ab initio* calculation. For example, differences between our DFT calculations and experimental $PA$ for formaldehyde, formic acid, methanol, ketene, acetaldehyde, ethanol, acetone, propanol, propionic acid and butanol are below 1%, in contrary to the HF results, where differences are

higher−from about 1.3% for ketene to about 3.7% for formic acid. For ketene, acetic acid, methyl acetate and ethyl acetate these differences are higher for both method. For example, for methyl acetate they amount to 8.8% and 5.7% in the HF and DFT calculations, respectively. It may be caused again by the fact that for molecules containing two oxygen atoms, two stable protonated isomers can exist and experimental $PA$ values have intermediate values between values of these isomers.

**Table 2.** Compared to experimental data proton affinities of oxygenated VOCs.

| Substance | Formula | $PA$ (kcal/mol) | | |
|---|---|---|---|---|
| | | Experiment[a] | Theory $C_3H_8O$ | |
| | | | HF/6-311G** | B3-LYP/6-311G** |
| Formaldehyde | $CH_2O$ | 170.4 | 174.83 | 168.81 |
| Formic acid | $CH_2O_2$ | 177.3 | 184.11 | 178.69 |
| Methanol | $CH_4O$ | 180.3 | 185.44 | 180.94 |
| Ketene | $C_2H_2O$ | 197.3 | 199.99 | 190.43 |
| Acetaldehyde | $C_2H_4O$ | 183.7 | 189.01 | 183.87 |
| Ethanol | $C_2H_6O$ | 185.6 | 189.85 | 186.20 |
| Glyoxal | $C_2H_2O_2$ | | 165.06 | 161.41 |
| Acetic acid | $C_2H_4O_2$ | 187.3 | 200.64 | 193.49 |
| Acetone | $C_3H_6O$ | 194.0 | 198.73 | 193.16 |
| Propanol | $C_3H_8O$ | 188.0 | 192.14 | 188.94 |
| Propargyl alcohol | $C_3H_4O_2$ | | 184.06 | 183.00 |
| Acrylic acid | $C_3H_4O_2$ | | 182.57 | 187.61 |
| Propionic acid | $C_3H_6O_2$ | 190.5 | 195.76 | 190.76 |
| Methyl acetate | $C_3H_6O_2$ | 191.1 | 209.69 | 202.64 |
| Butanol | $C_4H_{10}O$ | 188.6 | 192.16 | 189.60 |
| Ethyl acetate | $C_4H_8O_2$ | 190.7 | 207.13 | 201.06 |
| Pentanol | $C_5H_{12}O$ | | 188.66 | 188.91 |
| Hexanol | $C_6H_{14}O$ | | 191.25 | 188.73 |

[a]$PA$ was taken from NIST data compilations [17], see references therein.

## 4 Conclusions

Results of *ab initio* calculations of proton affinities for selected organic compounds by Hartree-Fock method with 6-311G** molecular orbital basis set are in good agreement with experimental data; this agreement is even better if the Density Functional Theory in B3LYP/6-311G** approach is used. However, different conformers should be taken into account in geometrical optimisation of some molecules. For hydrocarbons the proton affinities rise with the number of carbon atoms; for alkenes are higher than for alkanes; for oxygen containing molecules are generally higher than for hydrocarbons; for alcohols they change little, ranging between 180 and 190 kcal/mol, almost independently from the number of carbon atoms. Moreover, calculations showed that protonated alkanes can undergo decomposition with detachment of $CH_4$ molecule.

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