ajer.0000.12-17

Protonation in Benzyl Alcohol: Different Proton Affinities, Same Neutral Molecule

Emmanuel E. Etim[1*],

[1]*Department of Chemical Sciences, Federal University Wukari, PMB 1020, Wukari, Taraba State, Nigeria*

Oko Emmanuel Godwin[1],

[1]*Department of Chemical Sciences, Federal University Wukari, PMB 1020, Wukari, Taraba State, Nigeria*

SulaimanAdeoye Olagboye[2]

[2]*Department of Chemistry, Ekiti State University, Ado -Ekiti, Nigeria*

M. E. Khan[3]

[3]*Department of Chemistry, Federal University Lokoja, Kogi State*

***livedna.net/profile.php?dna=234.8332**

ABSTRACT

Background & Objectives: Benzyl Alcohol (BA) has 6 possible protonated sites which give rise to 6 possible proton affinities for the same neutral molecule (BA). However, experimentally, only one proton affinity value is reported for BA but computationally, each possible protonated site can be specifically optimized and the proton affinity calculated for each protonated species.

Materials and Methods: In this study, quantum chemical calculations were carried out using GAUSSIAN 09 suite of programs. Five (5) different computational methods have been employed to calculate the proton affinity for each possible protonated analogue.

Results: The results obtained are compared with the experimental value in order to determine the protonated analogue that corresponds to the experimental value and which is thermodynamically more favored. It was found that the best site for the protonation of BA is via the C7 atom as it corresponds more to the experimental value and also found to be more stable.

Conclusion: Generally, the best computational methods for the calculation of the PA values of BA was observed to be B3LYP/6-311++G** but on the basis of the best site of protonation G4 method happened to be the best computational method.

Keywords: Benzyl Alcohol (BA); Proton Affinity (PA); Protonation; Computational methods; Ab-initio; thermodynamics.

1. Introduction

Benzyl Alcohol (also known as benzenemethanol, alpha-toluenol or phenylcarbinol) is a colorless aromatic alcohol consisting of benzenewith a hydroxymethyl substituent with a molecular formula of $C_6H_5CH_2OH$ or C_7H_8O as shown in Fig.1 below.

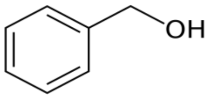


Fig.1:Structure of Benzyl Alcohol (BA)

BA finds application as solvents for paints, waxes, inks, Lacquers, shellacs,dyes and resins. As Fragrance and preservatives in soap, perfume, e-cigarettes.it also acts as insects repellants and a developer for photographic films.BA also finds application in health[1,2].It several usefulness have been attributed to its polarity, low toxicity, low vapor pressureand solubility in other solvents like water, alcohols and diethylether.

BA can be prepared or produced via the following path (a)Hydrolysis of toluene via benzyl chloride, shown in equation 1[3]. (b) Hydrogenation reaction of benzaldehyde equation2 and (c) The reaction of phenylmagnesium bromide with formaldehyde (Grignard reagent)[4]

$C_5H_5Cl + H_2O \longrightarrow C_6H_5CH_2OH + HCl$……………..(1)

$C_6H_5CHO \xrightarrow{H_2} C_6H_5CH_2OH$……………………………. (2)

Just like other alcohols, BA is a precursor for most esters as it undergoes esterification reaction with carboxylic acid to form esters, equation 3[5].

$PhCH_2OH + HOAc \xrightarrow{catalyst} PhCH_2OAc$………………………… (3)

It undergoes deprotonation reaction to form a benzylate anion and also undergoes a Ritter reaction with acrylonitrile to yield benzyl acrylamide as shown in equation (4)[6].

$C_6H_5CH_2OH + CH_2{=}CHCN \longrightarrow C_6H_5CH_2NHCOCH{=}CH_2$……………… (4)

Protonation simply refers to the resultant change in charge and mass of an atom, molecule or an ion brought about by the addition of a proton. The phenomenon “protonation” is quite different from “hydrogenation” in which the charge of the protonated specie is unaffected and so should not be misunderstood for protonation.

Proton Affinity (PA, E_{pa}) is the energy (Enthalpy) released in a reaction between a specie (anion,neutral atom or molecule) and a proton in the gas phase. This entails that when proton is added to specie in gas phase (protonation), energy is released (proton affinity). It is usually represented by the general equation: $PA\ (M) = \Delta_f H^0\ (M) + \Delta_f H^0\ (H^+) - \Delta_f H^0\ (MH^+)$……………(5)

Where $\Delta_f H^0$ represent enthalpies of formation[7].

The relationship between the PA of an acid /base and its strength was reportedly recorded by Poad[8] were they pointed out that if in the gas phase the proton affinity is higher, the base will be stronger while the conjugate acid will be weaker.the finding included that the strongest known base is Orthodiethynylbenzenedianion with an E_{pa} = 1843 kJmol^{-1} and Hunter and Lias[9]recorded the weakest known base,helium atom with E_{pa}= 177.8kJmol^{-1}. It's quite obvious that homonuclear species like $O_{2,}H_2$ have just one PA, hetero-nuclear species can have more than one PA e.gSiO_3 with two possible PAs, SCO with three protonation sites, as reported by a team led by Etim*et al.*[10,11], Toluene with four PAs[12] and phenol with two PAs[13,14].

One great application of PA in modern sciences lies in our quest to understand and explore the interstellar medium (ISM), one way of achieving this is by the study of the PAs of such molecules since their presence have been detected in the ISM[15,16,10,11].

Two basic methods are known for the determination of the PA of specie; experimental and computational approaches:

Experimental Approaches: this is an objective scientific known method which uses kinetic or thermodynamic data such asenthalpy change and the equilibrium constants in a proton transfer reaction. Some of the measurement techniques employed in this method include; High Pressure Mass Spectroscopy (HPMS)[17], Ion Mobility Spectrometry (IMS)[18,19], Flame Ion Mass Spectrometry (FIMS), Selected Ion Flow Tubes (SIFT), Iion Cyclotron Resonance (ICR) Spectrometry and Knudsen Cell Mass Spectrometry (KCMS)[20]. HPMS, SIFT, ICR are suitable for determining the PA of low temperature molecular species e.g organic compounds. KCMS is suitable for metallic compounds which decomposes at a lesser temperature while FIMS for metallic compounds which decomposes at a high temperature.

Computational Approach:Owing to difficulties in obtaining PAs experimentally gives rise to the computational approach. Uses the Ab-initio methods (which is based on quantum mechanics) or semi-empirical methodto used to obtain the PA via computer simulations. The ab-initio method is an approximate chemical calculationbased on theoretical principles independent of experimental data which enables solution of chemical parameters of the Schrodinger equatione.g electron density or energy from which PA is calculated. Different types of Ab-initio methods such as HF/6-311++G**, B3LYP/6-311++G**, MP2/6-311++G**, MP2/cc-pVDZ, G_4[21] have enabled researchers predicted structures, interactions and properties of systems accurately or approximately. For examples, Etim[10,11]computationally predicted the PA of SO_3 to be 140.2 kcal mol^{-1} using the B3LYP/6-311++G** level of theory, meanwhile the experimental value is 140.6 kcal mol^{-1}. In their ab-initio study of carbonylsulfide CSO. They again made a veryPerfect prediction using the HF/6-311++G** method when compared to the experimental values where they predicted the PA of CSO to be 150.7 kcal mol^{-1} and the experimental value is 150.2kcal mol^{-1}.

These findings support the authenticity and accuracy of the Ab-initio methods and calls for their use in comparison with experimental data as a tool in deciding which could serve as an alternative, thus the aim of this work; BA, a molecule with six (6) possible protonated species, which one correspond to the reported experimental value? We therefore aim to specify the best site of protonation as the experimental procedure is deficient of such information.

Materials and Methods

All the electronic structure calculations (thermodynamic properties) for the required proton affinities were implemented using the Gaussian 09 suit of programs[22].Five(5) Ab-initio computational methods which include: Gaussian 04 (G_4) compound method, Hartree-Fock (HF) method,Becke, three-parameter, Lee-Yang-Parr (B3LYP) method, Moller-Plesset perturbation theory (MP2) at 6-311++G** bias set and Moller-Plesset perturbation theory (MP2) at cc-pVDZ basis set were used in carrying out the calculations

These methods were chosen based on experience from our previous studies[15,16,10,11] in which these methods were applied and accurate results were obtained. Also, the use of these methods is essential in monitoring how consistent or coherent the results are which will aid in determining the best method. The proton affinity (PA) is calculated as the difference in energy (Electronic Energy) between a neutral specie and its protonated analogue.

RESULTS and DISCUSSION

Table 1: Proton Affinity **(**PA)for Benzyl Alcohol (BA)

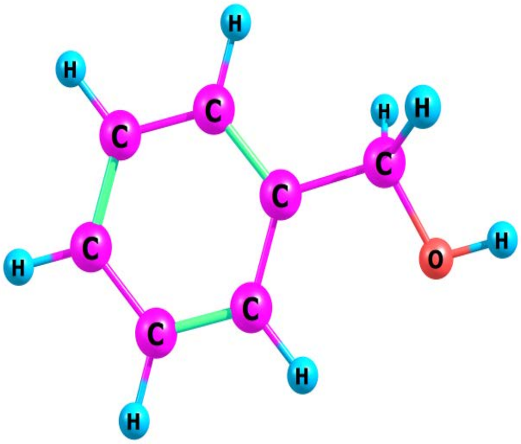
Molecule	**Protonation site**												
BA (C_7H_8O)		Proton attached to O atom		Proton attached to C_7 atom		Proton attached to C_2 atom		Proton attached to C_4 atom		Proton attached to C_6 atom		Proton attached to C_5 atom	
	x	PA (kcal mol^{-1})	Error	PA (kcal mol^{-1})	Error	PA (kcal mol^{-1})	Error	PA (kcal mol^{-1})	Error	PA (kcal mol^{-1})	Error	PA (kcal mol^{-1})	Error
	1	195.5	9.5	180.5	-5.4	188.2	2.2	195.1	9.1	190.8	4.8	196.1	10.1
	2	199.3	13.3	182.5	3.5	183.0	3.0	191.4	5.4	187.2	1.2	191.4	5.4
	3	191.5	5.5	174.5	-11.5	175.0	-11.0	180.9	-5.1	177.8	-8.2	180.9	-5.1
	4	194.9	8.9	178.2	-7.8	178.0	-8.0	184.2	-1.8	180.7	-5.2	184.2	-1.8
	5	200.4	14.4	189.0	3.0	188.7	2.7	197.3	11.3	192.9	6.9	197.4	11.4
	6	186.0	NA	186.0	NA	186.0	NA	186.0	NA	186.0	NA	186.0	NA

^{X}Method, ^{1}HF/6-311++G**, ^{2}B3LYP/6-311++G**, ^{3}MP2/6-311++G**, ^{4}MP2/cc-pVDZ, ^{5}G4, ^{6}Expt

Table 2: Sum of electronic and zero-point Energies at HF/6-311++G** levelfor protonated species

Parameter	Energy (Hartree/Particle)*					
	Protonation at O_1 atom	Protonation at C_7 atom	Protonation at C_2 atom	Protonation at C_4 atom	Protonation at C_6 atom	Protonation at C_5 atom
Zero-point correction	0.154046	0.152069	0.153613	0.152478	0.152694	0.152572
Thermal correction to Energy	0.161362	0..160296	0.160694	0.159785	0.160004	0.159848
Thermal correction to enthalpy	0.162307	0.161240	0.161638	0.160729	0.160948	0.160793

Thermal correction to Gibss Free Energies	0.122304	0.117289	0.122042	0.120444	0.120916	0.120869
Sum of electronic & zero-point Energies	**-344.848**	**-344.824**	**-344.836**	**-344.847**	**-344.840**	**-344.848**
Sum of electronic & thermal Energies	-344.840	-344.816	-344.829	-344.839	-344.833	-344.841
Sum of electronic & thermal Enthalpy	-344.839	-344.815	-344.828	-344.839	-344.832	-344.840
Sum of electronic & thermal Free Energies	-344.879	-344.859	-344.868	-344.879	-344.872	-344.880



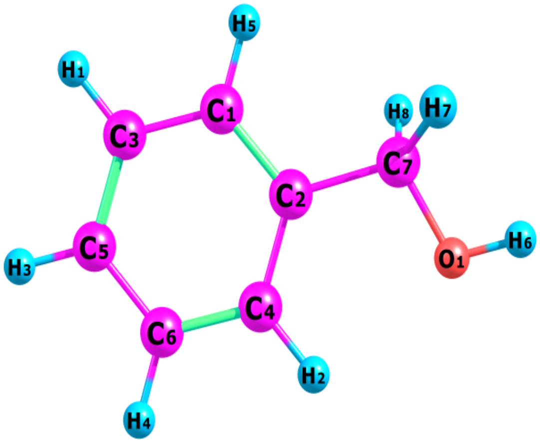
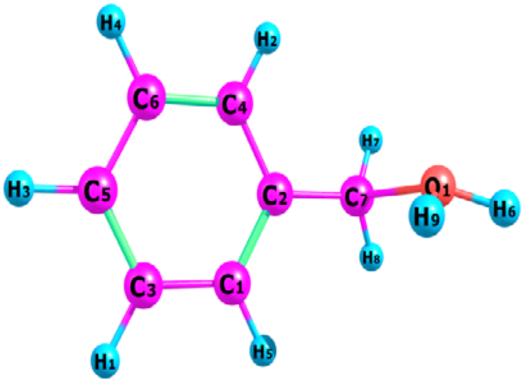


Fig. 2a: Optimized geometry of BA.Fig.2b: Optimized geometry of BA showing

the Numbering of atoms



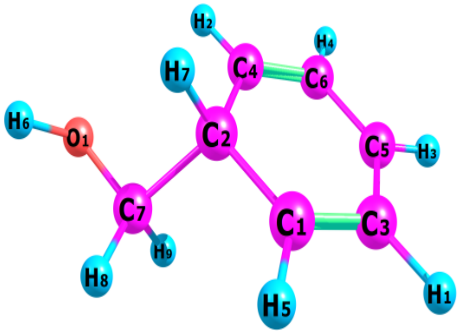


Fig.3a: Geometry for Protonation at O_1 atomFig.3b: Geometry for Protonation at C_7 atom

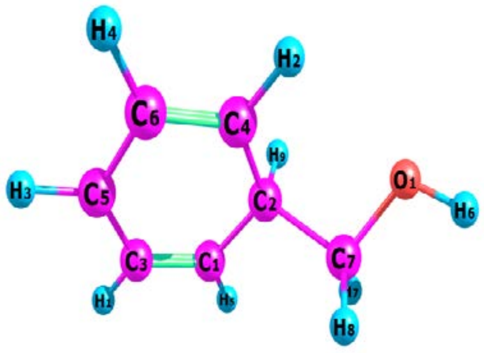


Fig.3c: Geometry for Protonation at C_2 atom

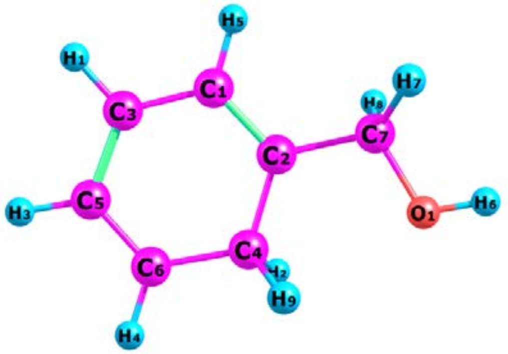


Fig.3d: Geometry of Protonation at C_4 atom

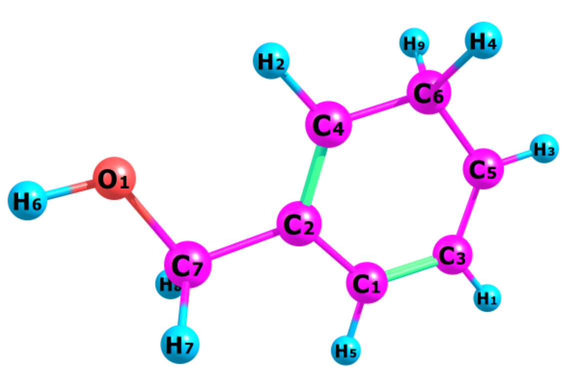


Fig.3e:Geometry for Protonation at C_6 atom

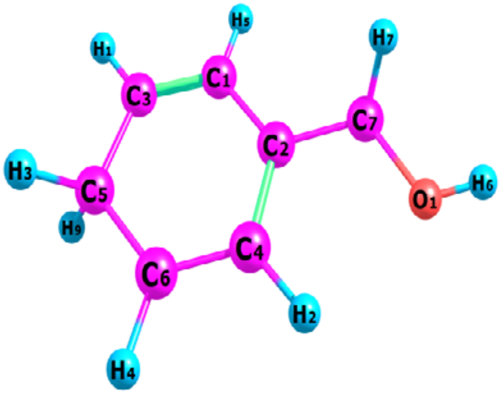


Fig.3f: Geometry for Protonation at C_5 atom

Table 1 present our calculated Proton Affinities (PAs) of Benzyl Alcohol(BA) in collaboration with its observed experimental value (186.0 kcal mol^{-1}) reported by the NIST website to aid our comparison.Fig.2a-b and Fig.3a-f depicts the optimized geometry of BA and its protonated analogues. BA has six possible protonated sites, giving rise to six possible proton affinities and six possible protonated analogues (species). The possible sites for the attachments of protons are: Proton attachment to O atom, to C_2 atom, to C_4 atom, to C_5 atom, to C_6 atom and to C_7 atom. C_1 an C_3 are not independently recorded as individual protonated site due to equivalency, C_6 is equivalent to C_3 and C_4 is equivalent to C_1.

i. **Proton attachment to O atom**: The second order Moller-plesset perturbation theory MP2 at 6-311G** levelof theory recorded the least error out of the 5 computational methods applied when proton was attached to O atom. All values obtained from the 5 computational methods were a little bit higher than the experimental values of 186.0 kcal mol^{-1}, only the MP2/6-311++G** method gave a value (191.5kcal mol^{-1}) more chosen to that of the experimental, an error of 5.5kcal mol^{-1}was recorded which happens to be the least of all the methods making it (MP2/6-311++G**) the method of choice for calculating PA in BA when proton is attached to the O atom. Generally, all the errors recorded where large. Only one method (MP2/6-311++G**) seem better.

ii. **Proton attached to C_7 atom**: With respect to the five computational methods under investigation, G_4 method obtained the best prediction with a PA value (189.0 kcal mol^{-1}) with just 3units higher than the experimental value. Proton attachment to C_7 has a good level of precision from all the computational methods. Generally, errors here too were large. Three of the five methods obtained better predictions (HF/6-311++G**, G_4 and B3LYP/6-311++G**) gave the least error. This protonated analogue appeared more stable than via O atom.

iii. **Proton attached to C_2 atom:** on this site of protonation, there was also a high precision or closeness of all the computational methods to the experimental value. Three out of five of the methods including B3LYP/6-311++G**, G_4 and HF/6-311++G** gave the least errors in that order and as such giving the HF method priority when it comes to attaching proton at the C_2 atom in BA. This specie appeared to be stable too.

iv. **Proton attached to C_4***:*Two methods (MP2/cc-pVDZ and MP2/6-311++G**) happen to be the only methods with a prediction a bit closer to the experimental value (i.e 184.2kcal mol^{-1} and 180.9 kcal mol^{-1} respectively). This specie appeared to be less stable.

v. **Proton attached to C_6 atom***:*Generally, from all the computational methods applied in this work and from all calculations made on the various possible protonated sites, the B3LYP/6-311++G** gave the best prediction (187.2kcal mol^{-1}) at this site compared to experimental value of 186.0kcal mol^{-1}. A least error of 1.2 kcal mol^{-1} was recorded while the other computationalmethods appliedon this site of protonation gave predictions that are a bit away from the experimental value, thereby altering stability on this site.

vi. **Proton attached to C_5 atom:** Just as shown for C_4, PAs obtained when proton is attached to C6 gave values that are far more away from the experimental value when compared to when proton is attached to other sites. The value predicted by MP2/CC (184.2) happens to be the only value closer to the experimental (186.0) with an error of 1.8 in magnitude. A critical study of stability via the value shows protonation on this site to be very much less stable.

From the above proceedings (discussion on the six possible protonated site with respect to the result obtained from the 5 different methods and their errors), we have elucidated and simplified the process of understanding our findings that theB3LYP/6-311++G** gave a better prediction of the PA of BA at the C6 analogue compared to every other computational methods implemented (with a prediction of 187.2kcal mol^{-1} as against 186 kcal mol^{-1} of the experimental value). On the basis of the protonated analogues or site of protonation, PAs obtained when proton is attached to O, C_4, C_5 and C_6 were unduly wide away from the experimental value, this entails the difficulty of protonation and the unstable nature of those protonated analogues, thus leaving us with species with proton at C_7 and C_2. But a critical look at Table 2, we noticed that protonation at C_7 was more favored than protonation at C_2 atom, this reveal that PA was best predicted when proton is attached to the C_7 atom since it is thermodynamically more stable and has values closer to the experimental observed value implying that both experimental and PA values for the specie correspond more. The results from our calculated PA values for BA therefore reveals that protonation via carbon atom (A site that is less electronegative and with less electron density) is better than protonation via the oxygen atom (which is more electronegative and with more electron density. As can be seen in Table 2,a stability checks shows that out of the five carbon sites, protonation at the C_7 atom was more favored and PA corresponds to a site that is thermodynamically more favored[23]. In extension, this finding also supports our previous work on Carbonyl sulfide CSO that electro negativity is not a good standard of judgment in predicting the protonation site of a molecule[10].

Conclusion

Five different computational methods have been applied in studying the protonation of Benzyl Alcohol (BA) with the aim to figure out the best site of protonation. the results obtained from the five different computational methods and their errors coupled with their thermodynamic stability checks reveals that the best site of protonation is through Carbon atom particularly the C_7 atom which is less electronegative and with less electron density since this protonated analogue was found to be more stable and corresponds to the experimentally obtained value, and that electronegativity is not a good standing point in predicting the site of protonation of a molecule.

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