HYDROXIDE, PROTON AND SWITTERIONIC WATER ADSORPTIONS ON CLOSED SINGLE-WALLED CARBON NANOTUBES

Raina Wanbayor, Vithaya Ruangpornvitsuti

Supramolecular Chemistry Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University 10330, Bangkok, Thailand

Abstract

The adsorptions of hydroxide ion, proton and water on the closed armchair (5,5) single-walled carbon nanotube (SWCNT) of sizes C40+C20n, n = 2 and 3 were studied using Hartree-Fock and two-layered ONIOM(MO:MO) methods. adsorption energies of proton and hydroxide ion on the C40+C40 SWCNT are -224.71 and -144.77 kcal/mol, at the HF/3-21G level and -194.45 and -122.65 kcal/mol, at the ONIOM(B3LYP/6-31G(d):AM1) level, respectively. The adsorption energies of hydroxide ions on the protonated SWCNT are -222.96 kcal/mol at the HF/3-21G level for C40+C40 and -204.91 kcal/mol at the ONIOM(B3LYP/6-31G(d):AM1 level for C40+C60, respectively. Based on the HF/3-21G computations, the interaction energies of the protonated, hydroxylated and zwitterionic-water added SWCNTs as C40+C40 type with a water molecule are -14.05, -13.65 and -14.97 kcal/mol, respectively.

Introduction

Single-walled carbon nanotubes (SWCNTs) that consist of a graphene sheet wrapped to form a cylinder, are a material that has been extensively studied both experiment and theoretical. The structures of SWCNTs are represented by a chiral vector Ch = na1 + ma2 symbolized as (n,m), where a1 and a2 denote equivalent lattice vector of graphene sheet if n = m, (n,n) nanotubes are called armchair. In particular, adsorption on the surface of SWCNTs continues to be an intriguing and important subject because of its wide potential applications in many respects. These theoretical results suggest that water adsorbed on hydroxylated graphite surface and SWCNTs to form adsorbed -H and -OH groups. In this study, we carried out the adsorption of hydroxide, proton and water on sidewall of SWCNT using Hartree-Fock and two-layered ONIOM(MO:MO) methods.

Methods

Geometry optimization of various sizes of SWCNTs, their complexes with adsorbents were performed using ab initio Hartree–Fock (HF) with 3-21G basis set and the two-layered ONIOM(MO:MO) approach using B3LYP/6-31G(d) as high model and semiempirical such as PM3 and AM1 methods were tested as low model. The two-layered ONIOM(B3LYP/6-31G(d):AM1) were mainly used in all computations. Based on the clusters for high model of the ONIOM, two different models by selecting pyrene-like area (C16) and C7+pyrene+C6-like area (C23) as model 1 and 2 have been employed in the computations.

The strain energies of studied SWCNT based on various reactions were evaluated at the HF/3-21G level. Thermodynamic properties for all the reactions were obtained by frequencies calculations at the two-layered ONIOM(B3LYP/6-31G(d):AM1). All calculations were performed with the GAUSSIAN 03 program.

The standard enthalpy ΔH_{298} and Gibbs free energy changes ΔG_{298} of all transformation reactions between the nitrosamine isomers have been derived from the frequency calculations at th eHF/3-21G level of theory.

Results and discussion

The structure optimizations for the closed armchair (5,5) single-walled carbon nanotube (SWCNT) of sizes C40+C40 and C40+C60 and their complexes were carried out at the HF/3-21G and ONIOM(B3LYP/6-31G(d):AM1) levels of theory. The HF/3-21G-optimized structures of C40+C40 SWCNT and C40+C60 SWCNT are shown in Fig 1.

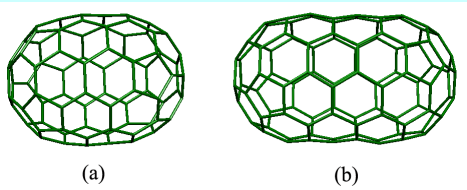

Fig. 1. Structural models of the closed armchair (5,5) SWCNT of sizes (a) C40+C40 and (b) C40+C60.

The reaction energies of proton, hydroxide ion of protonated SWCNT and interaction energies of protonated, hydroxylated and zwitterionic-water addition on the closed armchair (5,5) SWCNT were shown in Table 1. Based on HF/3-21G and ONIOM(B3LYP/6-31G(d):AM1), the interaction energies of zwitterionic-water addition on SWCNT of sizes C40+C40 and C40+C60 are -14.97 and -9.82 kcal/mol respectively as shown in the Fig 2.

Table 1 The reaction energies of proton, hydroxide ion of protonated SWCNT and interaction energies of protonated, hydroxylated and zwitterionic-water addition on the closed armchair (5,5) SWCNT

Features	ΔE (Kcal/mol)			
	HF/3-21G,	ONIOM(B3LYP/6-31G(d):AM1)		
	C40+C40	C40+C40 [a]	C40+C40 [b]	C40+C60 [b]
CNT	-3012.17	-614.11	-1113.33	-1225.93
CNT-H^+	-224.71	-194.45	-188.62	-202.28
CNT-OH^-	-144.77	-112.65	-[d]	-107.62
CNT-$H^+\cdots OH^-$	-221.13	-222.96	-213.69	-204.91
CNT-$H^+\cdots$W	-14.05	-11.27	-10.65	-9.26
CNT-$OH^-\cdots$W	-13.65	-11.45	-[d]	-9.18
CNT-H.OH···W	-14.97	-11.14	-10.26	-9.82

[a] The pyrene-like area was treated as high layer.
[b] The C7+pyrene+C6-like area was treated as high layer.
[c] No convergency is found.

Table 1 The thermodynamic quantities were obtained by ONIOM(B3LYP/6-31G(d):AM1) in the Table 2. The adsorptions of hydroxide, proton and water on the sidewall of closed armchair(5,5) (SWCNT) are chemisorption.

Features	C40+C40 SWCNT [a]			C40+C60 SWCNT [b]		
	ΔE	ΔH_{298}	ΔG_{298}	ΔE	ΔH_{298}	ΔG_{298}
CNT-H^+	-187.47	-187.54	-187.65	-195.50	-195.36	-195.62
CNT-OH^-	-109.59	-110.57	-100.15	-105.01	-105.93	-95.64
CNT-$H^+\cdots OH^-$	-214.74	-233.25	-205.22	-200.09	-201.22	-192.50
CNT-$H^+\cdots$W	-10.19	-9.99	-2.85	-8.12	-7.94	-1.05
CNT-$OH^-\cdots$W	-8.95	-9.50	0.01	-6.94	-7.25	1.38
CNT-H.OH···W	-8.92	8.15	-0.41	-7.93	-8.09	0.03

[a] The pyrene-like area was treated as high layer.
[b] The C7+pyrene+C6-like area was treated as high layer.

The thermodynamic quantities obtained at the ONIOM(B3LYP/6-31G(d):AM1) are listed in Table 2. The adsorptions of hydroxide ion, proton and zwitterionic-water the sidewall of closed armchair(5,5) SWCNT as chemisorption and their mono hydrations as physisorpption were found.

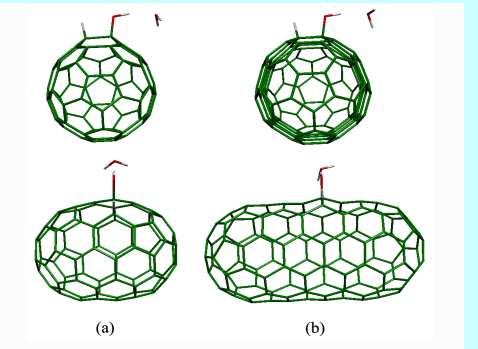

Fig. 2. The ONIOM(B3LYP/6-31G(d):AM1)-optimized structure of zwitterionic-water addition on the closed armchair (5,5) SWCNT of sizes (a) C40+C40 and (b) C40+C60. The above and below figures show their front and side views.

Conclusions

The reaction energies of protonation, hydroxylation, and zwitterionic-water addition on the sidewall of closed armchair (5,5) single-walled carbon nanotube (SWCNT) of sizes C40+C40 and C40+C60 and their binding energies with water and their thermodynamic quantities were obtained, strain energies of the adsorption-state SWNTs obtained are within the range of 6.30-33.87 kcal/mol.

References

[1]. Collignon, B.; Hoang, P.N.M.; Picaud S.; Rayez J.C. (2005) *Chem. Phys. Lett.* **406**, 430.
[2]. Ellison, M. D.; Good, A. P.; Kinnaman, C. S.; Padgett, N. E. (2005) *J. Phys. Chem. B.* **109**, 10640.

Acknowledgements

This work was financially supported by the National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Thailand.