

Theoretical Study of Addition Reaction of Carbene and Zigzag Single-walled Carbon Nanotube

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ABSTRACT

The reaction mechanism between (H₂C) and (7, 0), zigzag single-walled carbon nanotubes (ZSWCNTs) on two different orientation of C-C have been studied by semi empirical AM1 method. The activation barriers of (H₂C) adding to (7, 0) ZSWCNT are computed and compared. The effects of diameters of zigzag SWCNT on their binding energies were studied.

Keywords: CNT; Transition state; Carbene reaction

INTRODUCTION

The discovery of carbon nanotube (CNTs) has immediately followed the synthesis of fullerene in macroscopic quantities [1], intense research has been done to investigate their remarkable properties [2-4], and various production methods have been developed. A wide range of application is foreseen for these nanoscopic object, which include nano electronics [5, 6], chemical sensing [7,8], composite materials with improved properties [9,10] and etc. However, the large scale use of carbon nanotubes is still limited by the high production cost [11]. CNTs consist of graphite sheets, which have been rolled up into a cylindrical shape. The length of CNTs is in the size of micrometers with diameters up to 100 nm. Where mono layer is divided into three kinds based on how they will be rolled, defining with two characteristics (n,m). If n=m, nanotube is armchair, if n=0, nanotube is zigzag and if n,m ≠ 0, then nanotube is chair [12-16]. Single walled carbon nanotubes

(SWNT) are leading to the development of new nanotechnologies. CNTs form bundles, which are entangled together in the solid state giving rise to a highly complex network. Depending on the arrangement of the hexagon rings along the tubular surface CNTs can be metallic or semi conducting. Because of their extraordinary properties, nanotechnological application, such as fillers in polymer, matrixes, molecular tanks, bio sensors and many others the fictionalization process is the most promising strategy for overcoming these difficulties. Several functional groups have been successfully attached to the nanotubes, making these functionalized tubes very promising for application in catalysts support, gas storage and components in high performance composites [17, 18]. In this study, there were examined simulation of initial structure of zigzag carbon nanotube(7,0), and their reactive transition state using semi empirical methods with examination of

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energies of reactant, product and the structure of transition state by changing the carbene bond position on the nanotube at 298.15 K and 1 atm pressure in the calculation level of AM1.

COMPUTATIONAL DETAILS

In this study, the geometry optimization of the nanotube leading to energy minima were achieved by using AM1 method the initial geometry of carbene and carbon nanotube structure was excerpted from Hyperchem Library and Gauss View all these computations were performed by using Gaussian 98 We optimized the geometry of the reactants (CH_2 , (7,0) ZSWCNT($\text{C}_{70}\text{H}_{14}$) along with the reaction products between CH_2 and ZSWCNTs, i.e.,

Then the transition states (TSs) of CH_2 forming cycloaddition isomers on (7,0) were found. Frequency calculations have been performed for the reactants, TSs and products mentioned above in order to determine their stabilities. Intrinsic reaction coordinates were also calculated to confirm the correctness of the TSs.

RESULTS AND DISCUSSION

The addition of CH_2 to C-C vertical bonds of ZSWCNT (7,0) (Fig. 1) forms closed CH_2 cycloaddition isomers, respectively. The side views of the structures of reactants, TSs and products are shown in Fig. 1 and 2, and their thermodynamic geometry parameters is listed in Tables 1.

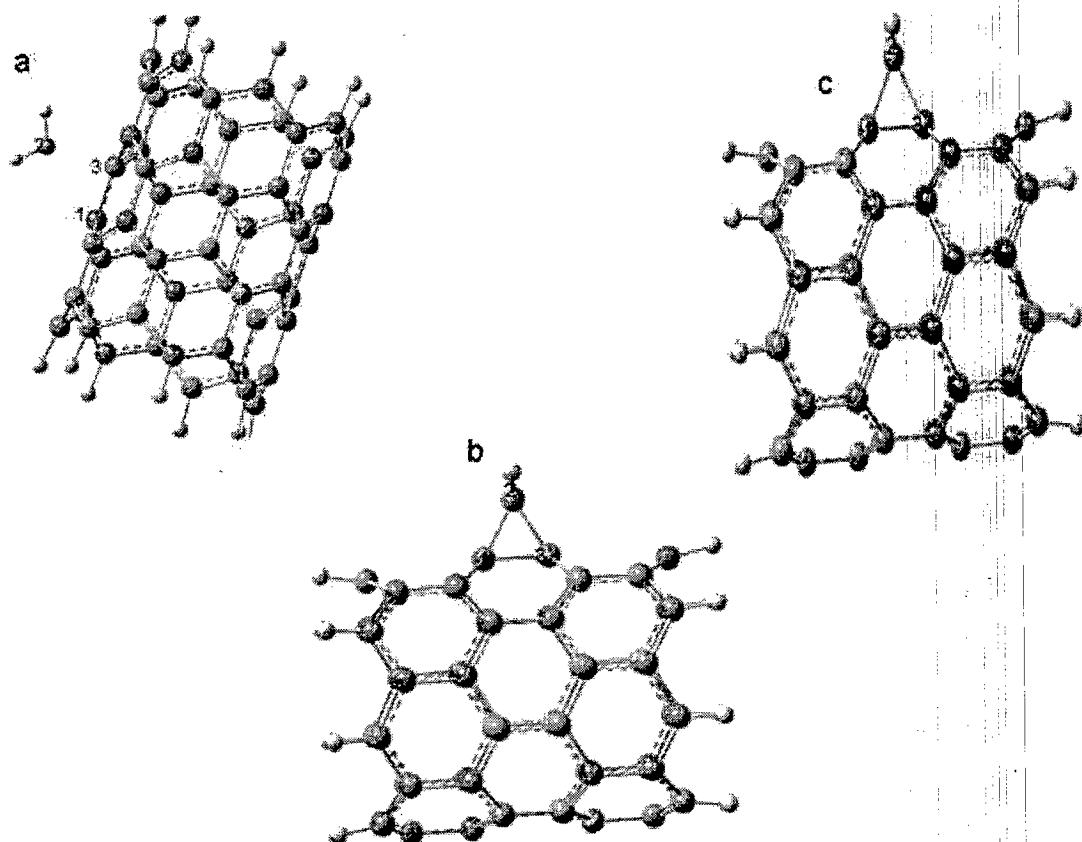


Fig. 1. AM1 Optimized geometry structures of (a) reactants, (b) TS and (c) product of the addition of CH_2 to the C-C vertical bond.

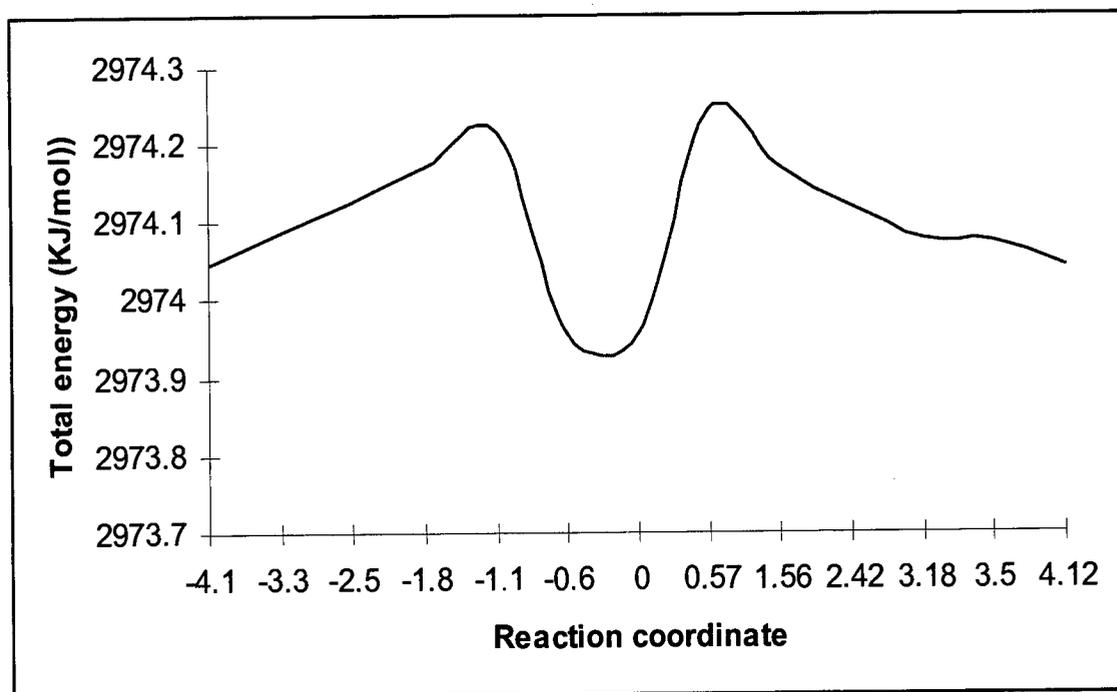


Fig.2. Intrinsic reaction coordinates (IRC) of the addition of CH_2 to the C-C vertical bond of (7,0) calculated by AM1 method.

Table 1. Electronic energies, ΔE^0 , enthalpies, ΔH^0 , and free energies, ΔG^0 , activation electronic energies, ΔE^* , activation enthalpies, ΔH^* , and activation free energies, ΔG^* , (kJmol^{-1}) at vertical bond for reaction between carben and side wall of ZSWCNT

ΔE^0	ΔH^0	ΔG^0	ΔE^*	ΔH^*	ΔG^*
-348.702	-349.748	-349.748	41.651	40.877	40.877

Table2. Structure parameter in reaction pathway between carbene and side wall of ZSWCNT at vertical bond in Fig.1

bond length($^{\circ}\text{A}$)	GS1	TS	GS2
r_{12}	3	1.50026	1.5025
r_{32}	3	1.50196	1.50047
r_{13}	1.42	1.54416	1.54378
bond angle($^{\circ}$)			
$\angle \text{C1-C2-C3}$	61.89	61.90643	61.8716

The addition of CH_2 to C-C diagonal bonds of ZSWCNT (7,0) (Fig. 2) forms closed CH_2 cycloaddition isomers. The side views of the

structures of reactants, TSs and products are shown in Fig. 3 and 4, and their thermodynamic geometry parameters is listed in Tables 2.

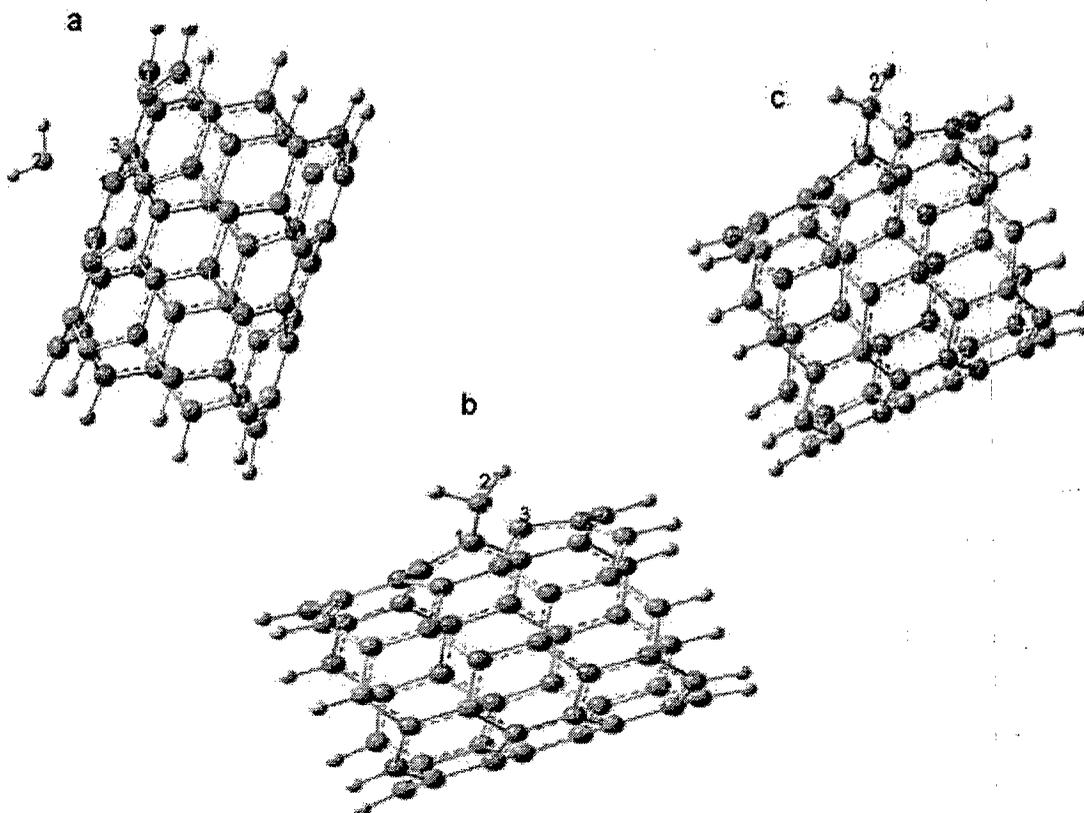


Fig . 3 . AM1 Optimized geometry structures of the reactants, TS and product of the addition of CH_2 to C-C diagonal bond of (7,0).

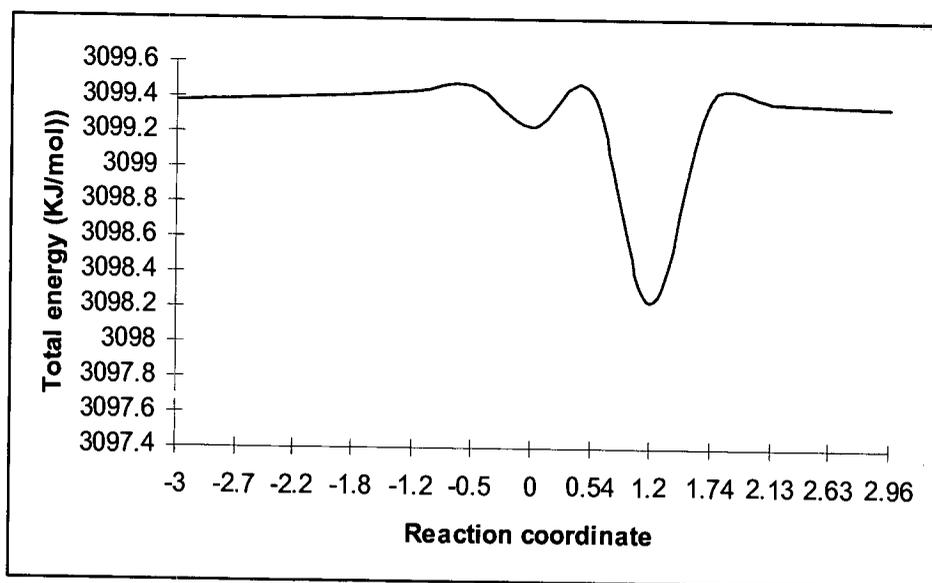


Fig . 4 . Intrinsic reaction coordinates (IRC) of the addition of CH_2 to the C-C diagonal bond of (7,0) calculated by AM1 method.

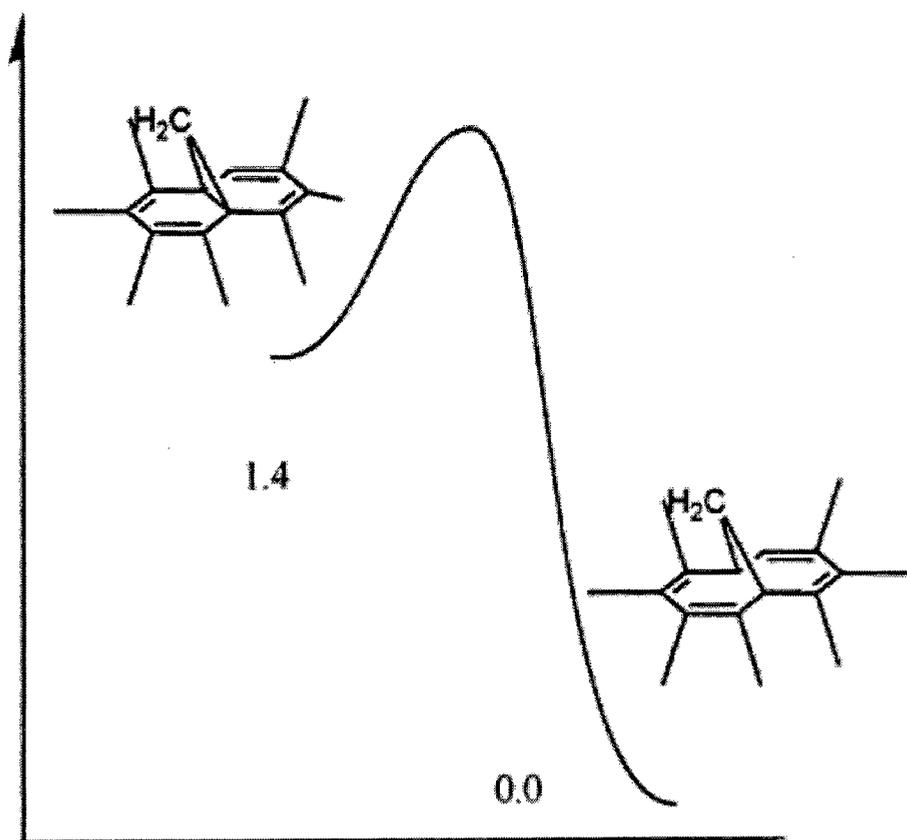


Fig .5. Sketch map of ring opening in cyclopropane (1.4 kJ.mol^{-1})

Table 3. Electronic energies ΔE^0 , enthalpies ΔH^0 and free energies ΔG^0 Activation electronic energies ΔE^* , activation enthalpies ΔH^* and activation free energies ΔG^* (KJ.mol^{-1}) at vertical bond for reaction between carben and side wall of SWCNT.

ΔE^0	ΔH^0	ΔG^0	ΔE^*	ΔH^*	ΔG^*
-454.788	-454.892	-649.135	-399.015	-400.08	-592.54

Table 4.Structure parameter in reaction pathway between carbene and side wall of ZSWCNT at Diagonal bond in fig3

bond length($^{\circ}\text{A}$)	GS1	TS	GS2
r12	3	1.4705	1.49056
r32	3	1.46904	1.48919
r13	1.41959	1.53	2.25208
bond angle($^{\circ}$)			
<C1-C2 -C3	97.87	98.356	98.19

Frequency calculation results show that the reactants and products have stable structures and only one imaginary frequency exist for C-C diagonal TS. The intrinsic reaction coordinates of CH₂ adding to C-C diagonal bond of (7,0) C₇₀H₁₄ indicates that TS connects the reactants and product.

Table 1 shows that ΔE^0 , ΔH^0 and ΔG^0 is --348.702, -349.748 and -349.748 (kJ.mol⁻¹) respectively and ΔE^* , ΔH^* and ΔG^* (kJ.mol⁻¹) is 41.651, 40.877 and 40.877 at vertical bond.

Table 2 shows that ΔE^0 , ΔH^0 and ΔG^0 is -454.788,-454.892 and -649.135 (kJ.mol⁻¹) respectively and ΔE^* , ΔH^* and ΔG^* (kJ.mol⁻¹) is -399.015,-400.08 and -592.54 at diagonal bond.

So the bond becomes longer from the reactant to TS and finally breaks in the product. The break of C-C diagonal bond can release the strain energy of the product. That is shown in Fig. 3. Strain force in cyclopropane cause ring opening and increasing stability in SWCNT structure .Fig 5. Therefore, Table 1 and 2 show that the interaction between CH₂ and C-C vertical bond is stronger than that between CH₂ and C-C diagonal bond. The heat of reaction for adding CH₂ to C-C vertical and diagonal bonds are -83.5919,-108.722 respectively. So reaction between CH₂ and diagonal bond is more exothermic than vertical bond.

The activation energies obtained by AM1 method calculation of CH₂ adding to C-C

diagonal and vertical bond are -108.697 and -83.3419 (KJ.mol⁻¹), respectively, indicating that the C-C diagonal bond has lower reactivity than C-C vertical bond. Probably the needs of more energy for the break of C-C vertical bond cause the formation of open isomer more difficult. However, the difference between the energy barrier of CH₂ adding to C-C diagonal and C-C vertical bonds of (7,0) is so very large[19].

CONCLUSION

Our theoretical study shows that whatever the bonds of ZSWCNT (7,0)CH₂ added to, the same reaction mechanism is obtained :

CH₂+ ZSWCNT → TS (unsymmetrical) → Products (closed cycloaddition isomer).

This is consistent with the results of reference [20]. When CH₂ is added to the C-C diagonal bond of (7,0), our investigation results show that the reaction mechanism is probably as below:

Reactants → Transition State 1 (TS1) → Closed Isomer → Transition State 2 (TS2) → product.

We presume that CH₂ forms cycloaddition isomer on the diagonal bond of (7,0) (energy barrier -108.69 (kJ.mol⁻¹) more readily than on that of vertical bond of (7,0) (energy barrier -83.3419 (kJ.mol⁻¹)). There for the larger strain energy of diagonal bond (7,0) makes the reaction easier.

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