

Note

Recombination of propargyl radicals to form benzene: A computational study

Hari Ji Singh* & Nand Kishor Gour

Department of Chemistry, DDU Gorakhpur University,
Gorakhpur 273 009, India

E-mail: hari_singh81@hotmail.com

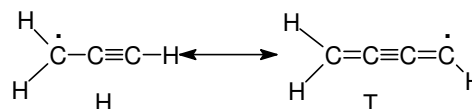
Received 1 May 2009; accepted (revised) 25 March 2010

Present study involves QCISD(T)/6-311G(d,p) level calculations to analyze reaction pathways during the recombination of propargyl radicals leading to the formation of benzene. A new path on the C_3H_3 recombination potential energy surface that connects 3,4-dimethylenecyclobutene (34DMCB) to benzene involving four-membered bicyclic compounds such as bicycle-[2.2.0]hexa-1(4),2-diene and bicyclo[2.2.0]hexa-2,5-diene have been determined. Geometries of all the species are optimized at HF/6-31G(d) level. All the stationary points along this path on the potential energy surface have been characterized. Single point energy calculation have been performed using QCISD(T) with 6-311G(d,p) basis set. Transition states are determined and characterized by the observation of only one imaginary frequency. Intrinsic Reaction Coordinate (IRC) calculation has also been performed in order to ascertain the existence of the transition states.

Keywords: Propargyl radical, HF, IRC, PES, 3,4-dimethylenecyclobutene

One of the intriguing problems always faced by combustion chemists during the flame or high temperature pyrolytic studies of hydrocarbon fuels is to find an explanation for the formation of aromatics and soot from low molecular weight gaseous species such as C_2H_2 , C_2H_4 , etc. Propargyl radical C_3H_3 (m/z 39) has been found abundantly in flames and it has also been detected during time-of-flight mass spectroscopic studies of many aliphatic fuels¹⁻⁴. The latter studies also detected peak at m/z 78. Modeling calculations performed on the m/z 78 profile envisaged the species as benzene. Thus, the main question raised is how do these aliphatic fuels which breakup to smaller fragments mostly C_2 and C_3 species at high temperature say 1500-2000 K undergo cyclization and form benzene. C_3H_3 is a resonantly stabilized free radical and is believed to play a critical role in the formation of aromatic hydrocarbons and

soot⁵⁻⁸. The unpaired electron present in C_3H_3 radical is delocalized and spread out over two or more sites. As a result of the delocalization of the unpaired electron, these free radicals are stabilized and normally form weaker bonds with stable molecules^{9,10}. Such weakly bonded addition complexes are not easily stabilized by collisions at high temperature, nor do they readily undergo rearrangement. In such a situation such radicals are relatively non-reactive and can reach high concentrations in flames. High concentrations and rapid rates at which such radicals may react with another constituent make an important route for the formation of higher hydrocarbons in flames. There is a possibility of the formation of other C_3H_3 isomers. Four such isomers viz., 2-propynyl (propargyl), 1-propynyl, cycloprop-1-enyl and cycloprop-2-enyl have been proposed to be thermally stable¹¹. Additional isomers may also be formed but these have been ruled out, being kinetically unstable¹¹. A recent computational study performed at a very high level utilizing electron correlation *via* second order Z-Averaged Perturbation Theory (ZAPT2) and primarily through coupled cluster theory by Wheeler *et al.*¹¹ reported the heat of formation of the different isomers of C_3H_3 and the calculated isomerization energies. The results show that propargyl has the lowest energy and thus the most stable amongst the four C_3H_3 isomers¹¹. The recombination of propargyl radicals is proposed to be one of most important reactions occurring in hydrocarbon flames^{5,6}. Depending on the reaction conditions, they may lead to the formation of a number of cyclic and chain hydrocarbons. It may be shown to exist in the following two resonating structural forms:



Out of these two resonating structures the structure marked as H is accepted to have a dominant one¹². These stabilized free radicals can combine in three

possible ways¹²⁻¹⁶ leading to the formation of C₆H₆ as shown below:

1. Head to head (HTH) → HC≡C—CH₂—CH₂—C≡CH
1,5-hexadiyne (15HD)
2. Tail to tail (TTT) → H₂C=C=CH—CH=C=CH₂
1,2,4,5-hexatetraene (1245HT)
3. Head to tail (HTT) → H₂C=C=CH—CH₂—C≡CH
1,2-hexadiene-5-yne (12HD5Y)

In the above recombination reactions CH₂ end of the propargyl is designated as the head (H) and CH as the tail (T) end. The path shown for the benzene formation *via* HTT recombination forming 12HD5Y has been extensively studied by Miller and Klippenstein¹⁵ and various transition states in the path following have been characterized. Thus, attention was focused to explore the path following HTH and TTT leading to the formation of benzene. Both HTH and TTT reaction paths lead to the formation of 3,4-dimethylenecyclobutene (34DMCB) as a stable species which has been reported to be the dead end.

In the present study it is attempted to explore the path for the formation of benzene from 3,4-dimethylenecyclobutene (34DMCB) using computational methods. The structures of all the species involved in the path are optimized and transition states characterized. Reaction energetics has also been studied.

Computational Details

Ab-initio calculations¹⁷ performed during the course of present investigation are done using the G03 package¹⁸. The geometries of all the species and the transition states involved have been optimized at Hatree-Fock¹⁹ level of theory using 6-31G(d) basis set²⁰. In order to get a refined and more accurate value of electronic energy of the molecule single point energy calculations are performed at quadratic configuration interaction QCISD(T)/6-311G(d,p)^{21,22} method which includes singles and doubles excitations and the contribution from triples excitations taken in a perturbative manner. QCISD(T) calculation is performed on geometries optimized at HF/6-31G(d) level. Electronic energies of various species involved are calculated and corrected for zero-point energies. The latter are obtained at HF/6-31G(d) level of theory. A scaling factor of 0.9135 is used for zero-point energy correction²³. In order to characterize the stationary points, vibrational frequencies were calculated on the optimized geometries. Absence of any imaginary frequency

during the frequency calculation shows that the stationary point obtained on the corresponding potential energy surface is the minimum that corresponds to the optimized structure. Transition states are identified by the presence of only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations²⁴ are performed at HF/6-31G(d) level of theory to ascertain the existence of the transition states.

Results and Discussion

The recombination products of propargyl following three different paths *viz.*, TTT, HTH and HTT forming 1245HT, 15HD and 12HD5Y respectively are shown in **Figure 1**. Optimized geometries of various species obtained at HF/6-31G(d) level is also shown in **Figure 1**. There is a plausibility of sigmatropic [1,3] H-transfer between these three recombined products and the path may follow 15HD → 12HD5Y → 1245HT. This possibility is ruled out with the fact that in thermal reactions 1,3 H shift must be antarafacial and this shift is impossible because a three-carbon chain is too rigid to allow the H atom to migrate in such cases²⁵. Therefore, the possibility of 15HD to undergo cyclization is minimum. Thus, the only path left for 15HD is to undergo isomerization to form 1245HT and this has been explored during the present study. The experimental studies performed by Tang *et al.*¹⁶ showed that all three isomers of C₆H₆ were present during the propargyl recombination with branching ratios of 44%(15HD), 38%(12HD5Y) and 18%(1245HT). In another experimental study Fahr and Nayk²⁶ showed that the formation of 15HD to the extent of 60%. The path following HTT forming 12HD5Y and subsequently to benzene on the propargyl recombination surface has been studied by Miller *et al.*¹⁵ and therefore this path has not been taken into consideration during the present study. One of the species formed by the path following HTH and TTT is 3,4-dimethylenecyclobutene (34DMCB). The subsequent isomerization and/or transformation of 34DMCB to other species/products have not been studied so far. In an earlier computational study performed on the PES of propargyl recombination it has been shown to be the dead end^{6,15}. In the present work the path from 34DMCB to benzene is explored. Zero point energy and electronic energy at HF/6-31G(d) level for the various species and transition states are recorded in **Table I**. Zero point energy corrected total energies for various species and transition states calculated at QCISD(T)/6-311G(d,p)

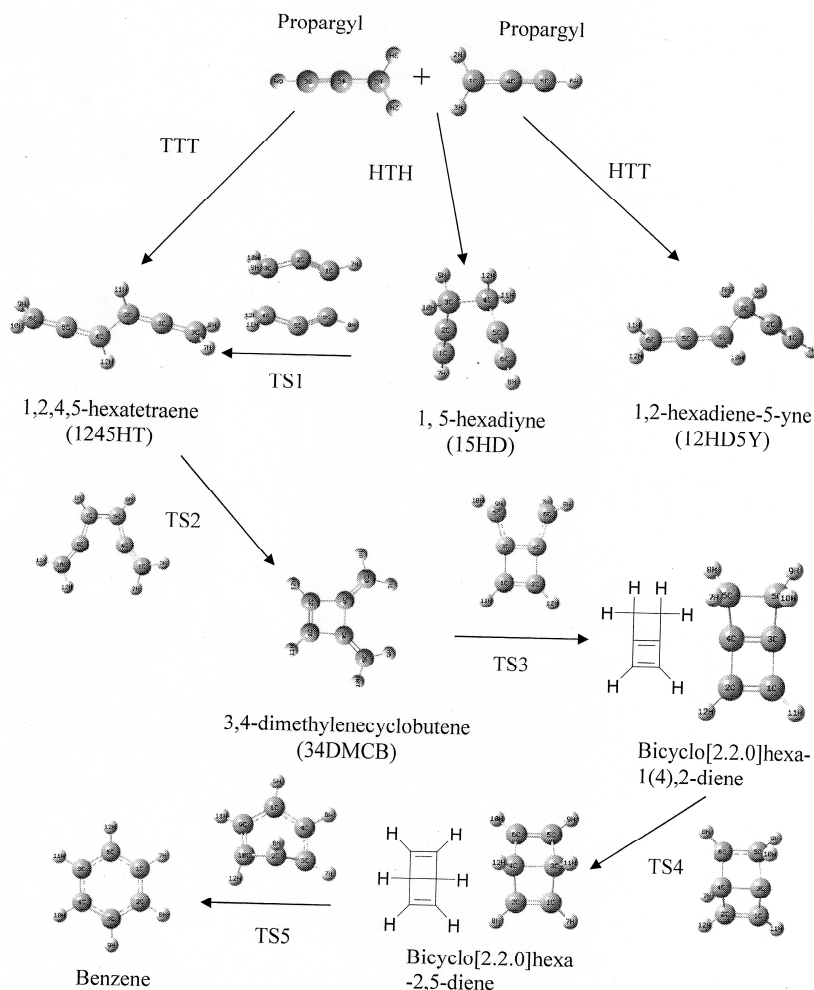


Figure 1 — Reaction pathways involved during the recombination of propargyl radicals and the path following 34DMCB to benzene

Table I — Zero point energy and electronic energy at HF/6-31G(d) for various species and transition states (Unit: hartrees)

Species/Transition states	ZPE	E _{ele}
Propargyl Radical	0.042571	-115.2506017
1,5-Hexadiyne(15HD)	0.102156	-230.5670522
1,2,4,5-Hexatetraene(1245HT)	0.100930	-230.5739857
3,4-Dimethylenecyclobutene(34DMCB)	0.103732	-230.5960778
Bicyclo[2.2.0]hexa-1(4),2-diene	0.103618	-230.4631333
Bicyclo[2.2.0]hexa-2,5-diene	0.105555	-230.5653187
Benzene	0.107674	-230.7031370
TS1	0.098809	-230.4650172
TS2	0.099721	-230.5035036
TS3	0.100819	-230.4013948
TS4	0.098444	-230.4001192
TS5	0.100337	-230.4826819

level are recorded in **Table II**. Energy barriers for different transition states along the present path are calculated from the data recorded in **Table II**. The barrier heights are recorded in **Table III**. Propargyl radical following HTH path directly combine to form 15HD. This further isomerizes to 1245HT involving a transition state TS1. The barrier to this transition is determined to be 37.6 kcal mol⁻¹. The stabilized open chain 1245HT undergoes cyclization forming a four-membered ring compound (34DMCB) through a transition state TS2. The optimized structures of TS1 and TS2 are shown in **Figure 1**. The barrier for the isomerization involving TS2 is calculated to be 30.8 kcal mol⁻¹. These isomerizations involving TS1 and TS2 were also shown by Miller *et al.*¹⁵ showing barriers to transitions as 35.4 and 29.6 kcal mol⁻¹ at

Table II — Zero point energy corrected total energies for various species and transition states calculated at QCISD(T)/6-311G(d,p) level*

Species/Transition states	E _{Total} (hartrees)
Propargyl Radical	-115.6663918
1,5-Hexadiyne(15HD)	-231.4299700
1,2,4,5-Hexatetraene(1245HT)	-231.4375967
3,4-Dimethylenecyclobutene(34DMCB)	-231.4569197
Bicyclo[2.2.0]hexa-1(4),2-diene	-231.3460070
Bicyclo[2.2.0]hexa-2,5-diene	-231.4352894
Benzene	-231.5542282
TS1	-231.3700927
TS2	-231.3885282
TS3	-231.3029847
TS4	-231.3182034
TS5	-231.3751492

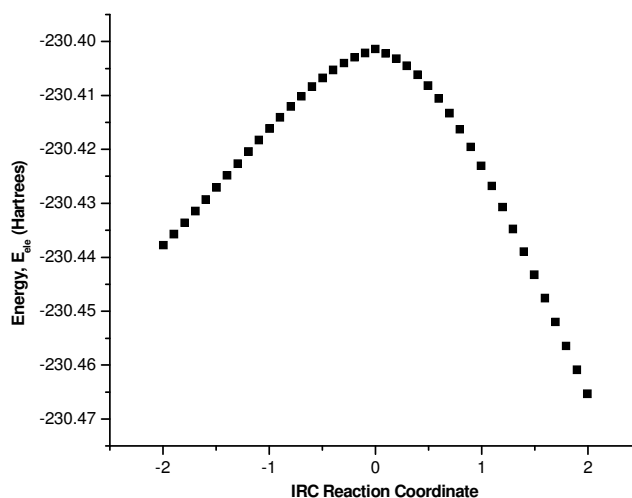
*A scaling factor of 0.9135 is used for correcting the ZPE calculated at HF/6-31G(d) level.

Table III — Calculated energy barriers for transition states. Details of the paths are shown in **Figure 1**.

Transition states	Energy barrier (kcal mole ⁻¹)
TS1	37.6
TS2	30.8
TS3	96.6
TS4	17.4
TS5	37.7

0 K respectively. This shows a good correspondence between the two independent calculations.

The path following 34DMCB to benzene which remained unexplored in earlier works^{6,15} is studied extensively during the present investigation and are shown in **Figure 1**. In a particular study²⁷ the formation of a four-membered bicyclo compound, bicyclo[2.2.0]hexa-1(4),2-diene had been shown to be involved from 34DMCB as an intermediate but the structural parameters of transition states involved in the path could not be determined. During the course of the present study extensive search was made to find the transition state for the formation of benzene from bicyclo[2.2.0]hexa-1(4),2-diene as proposed by Miller and Melius²⁷ but such a transition state could not be found on the potential energy surface. On the other hand the present investigation reveals that the path following 34DMCB to benzene does not proceed in a single step, instead it involves two steps as depicted in **Figure 1**. The additional intermediate during the

**Figure 2** — IRC plot for the transition state TS3 formed in the path 34DMCB → Bicyclo[2.2.0]hexa-1(4),2-diene

second step has been determined to be bicycle [2.2.0]hexa-2,5-diene also shown in **Figure 1**. This is in contradiction to the work proposed by Miller and Melius²⁷. The transition states TS3, TS4 and TS5 involved during the path following 34DMCB → Benzene are optimized. **Figure 1** also contains the optimized structures of these transition states. Frequency calculation performed on the optimized structures of each transition state shows the existence of only one imaginary frequency and these are TS3 (-932.1 cm⁻¹), TS4 (-1507.7 cm⁻¹) and TS5 (-1078.3 cm⁻¹). Vibrations pertaining to these imaginary frequencies were visualized by GaussView Program²⁸ and found to correspond to valid transition states. In order to ascertain the existence of transition state on the potential energy surface along the reaction path IRC calculations were also performed for each one of the transition states. IRC plots for TS3, TS4 and TS5 are shown in **Figures 2-4**. These plots clearly show that transition states connect the reactant and the product and there is a smooth transition.

The energy diagram for rearrangement of 15HD and 1245HT formed *via* HTH and TTT paths ultimately leading to the formation of benzene is shown in **Figure 5**. Energy barriers to various transitions as given in **Table III** are determined from the calculated electronic energy data of various species recorded in **Table II**. Energy barrier involved during the transition of 34DMCB to the first intermediate bicyclo[2.2.0]hexa-1(4),2-diene is determined to be 96.6 kcal mol⁻¹ while in an earlier study Miller and Melius²⁷ determined it to be

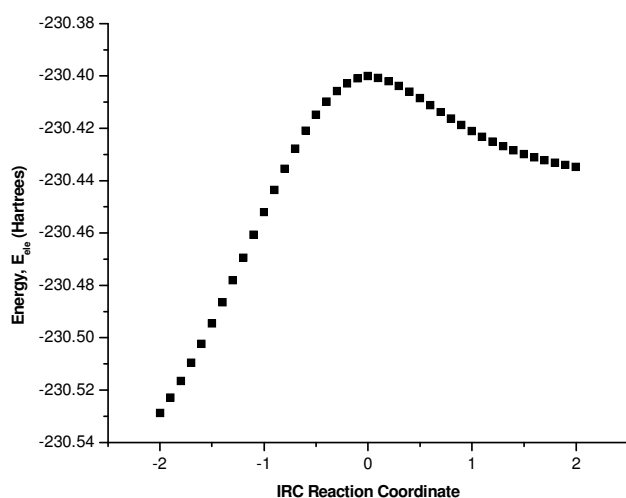


Figure 3 — IRC plot for the transition state TS4 formed in the path following Bicyclo-[2.2.0]hexa-1(4),2-diene $\rightarrow$ Bicyclo[2.2.0]hexa-2,5-diene

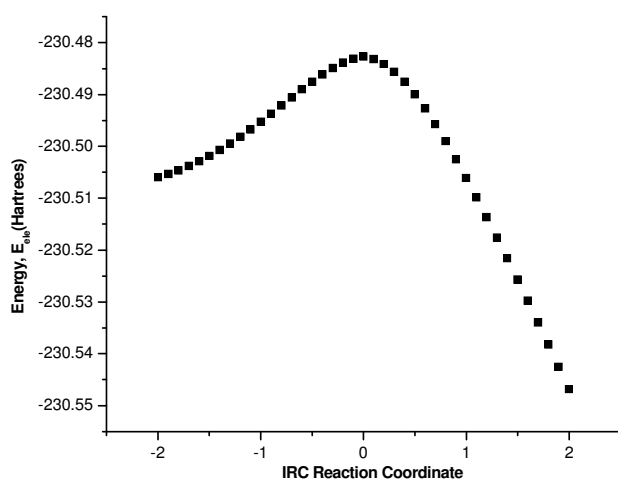


Figure 4 — IRC plot for the transition state TS5 formed in the path following Bicyclo[2.2.0]hexa-2,5-diene $\rightarrow$ Benzene

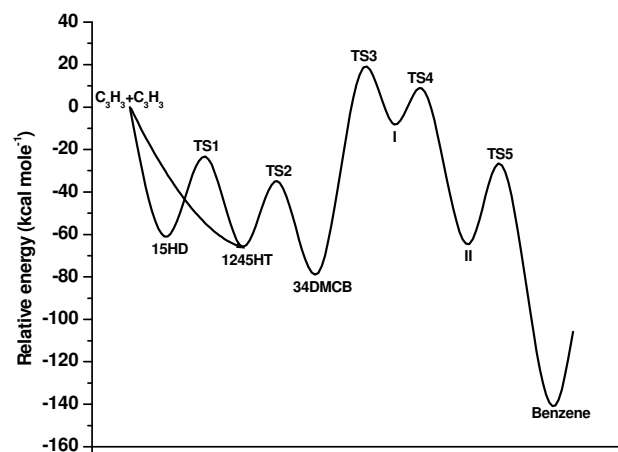


Figure 5 — Energy diagram for the propargyl's recombination path following 34DMCB to benzene. I. Bicyclo [2.2.0] hexa-1(4),2-diene, II. Bicyclo [2.2.0] hexa-2,5-diene

$\approx 82 \text{ kcal mol}^{-1}$ at 300 K. A part of this discrepancy may be attributed to the difference of temperature. The process $34\text{DMCB} \rightarrow \text{bicyclo}[2.2.0]\text{hexa-1(4),2-diene}$ (Intermediate I) will be highly endothermic and it is probably thermally driven. In such a case the transition state would correspond to more like the product that is intermediate I. An energy diagram for transition from propargyl radical recombination to benzene formation involving various transition states is shown in **Figure 5**. The most notable contribution of the present study is the exploration of the path connecting 34DMCB to benzene and the characterization of transition states involved during this transition.

Conclusion

The study of potential energy surface and structural determination of various species involved during the recombination reaction of propargyl radicals are quite informative because they provide an understanding of the possible reaction paths along with energies involved during the transformation. The potential energy diagram for the isomerization of 34DMCB to benzene explored during the present investigation elucidates a new path with the identification of transition states. Two new intermediates along the path following 34DMCB to benzene have been determined and transition states involved during this transformation are characterized.

Acknowledgement

The present study was supported by University Grants Commission, New Delhi under its Grants-in-Aid program for major research project sanctioned to HJS. Authors are thankful to UGC for providing research fellowships to NKG and BKM under its DSA-Program sanctioned to the Department of Chemistry, DDU Gorakhpur University.

References

- 1 Kern R D, Wu C H, Yong J N, Pamidimukkala K M & Singh H J, *Energy and Fuels*, 2, **1988**, 454.
- 2 Kern R D, Singh H J & Wu C H, *Int J Chem Kinet*, 20, **1988**, 731.
- 3 Wu C H & Kern R D, *J Phys Chem*, 91, **1987**, 6291.
- 4 Wu C H, Singh H J & Kern R D, *Int J Chem Kinet*, 19, **1987**, 975.
- 5 Miller J A & Melius C F, *Combust Flame*, 91, **1992**, 21.
- 6 Melius C F, Miller J A & Evleth E M, *Proc Combust Inst*, 24, **1992**, 621.
- 7 Miller J A, *Proc Combust Inst*, 20, **1996**, 461.

- 8 Richter H & Howard J B, *Prog Energy Combust Sci*, 26, **2000**, 565.
- 9 Slagle I R & Gutman D, *Proc Combust Inst*, 21, **1986**, 875.
- 10 Atkinson D B & Hudgens J W, *J Phys Chem A*, 103, **1999**, 4242.
- 11 Wheeler S E, Robertson K A, Allen W D, Schaefer III H F, Bomble Y J & Stanton J F, *J Phys Chem A*, 111, **2007**, 3819.
- 12 Miller J A & Klippenstein S J, *J Phys Chem A*, 105, **2001**, 7254.
- 13 Alkemade U & Homann K H, *Zeit Physik Chem*, 161, **1989**, 19.
- 14 Klippenstein S J & Miller J A, *J Phys Chem A*, 106, **2002**, 9267.
- 15 Miller J A & Klippenstein S J, *J Phys Chem A*, 107, **2003**, 7783.
- 16 Tang W, Tranter R S & Brezinsky K, *J Phys Chem A*, 109, **2005**, 6056.
- 17 Hehre W J, Radom L, Schleyer P V R & Pople J A, *Ab initio Molecular Orbital Theory*. (John Wiley and Sons, New York), **1986**.
- 18 Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A Jr, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honoda Y, Kitao O, Naki H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J. W, Ayala P Y, Morokuma, K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, AL-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C & Pople J A, *Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT*, **2004**.
- 19 Roothaan C C J, *Rev Mod Phys*, 23, **1951**, 69.
- 20 Gordon M S, Binkley J S, Pople J A, Pietro W J & Hehre W J, *J Am Chem Soc*, 104, **1982**, 2797.
- 21 Krishnan R, Frisch M J & Pople J A, *J Chem Phys*, 72, **1980**, 4244.
- 22 Feller D & Davidson E R, *Chem Rev*, 86, **1986**, 681.
- 23 Foresman J B & Frisch A, *Exploring Chemistry with Electronic Structure Methods*, 2nd Edn, (Gaussian Inc, Pittsburgh), **1996**, p. 64.
- 24 Gonzalez C & Schlegel H B, *J Chem Phys*, 94, **1990**, 5523.
- 25 Clayden J, Greeves N, Warren S & Wothers P, *Organic Chemistry*, (Oxford University Press, New York), **2001**, p. 955.
- 26 Fahr A & Nayak A, *Int J Chem Kinet*, 32, **2000**, 118.
- 27 http://www.anl.gov/PCS/acsfuel/preprint%20archive/Files/Merge/Vol-36_4-0007.pdf
- 28 Frisch A, Nielsen A B & Holder A J, *GaussView Users Manual*, Gaussian Inc, **2003**.