Kinetics of the Reaction of C_2H with C_2H_{2s}

Nitu

Research scholar

Department Chemistry

Baba Mast Nath University Rohtak

Abstract:-

In this theoretical research, the mechanism of the C_2H + C_2H_2 reaction is studied by high-level quantum-chemical methods, and kinetics of the reaction is investigated by statistical rate theories. High-level electronic structure calculation methods including M06-2X, CCSD(T), CBS-Q and G4 methods are employed to explore the doublet potential energy surface of the reaction and compute the molecular properties necessary for carrying out the statistical rate theory calculations. After locating stationary points of the reaction, steady-state approximation to the chemically-activated intermediates along with some statistical manipulations are applied to derive some practical integral equations for the rate constants of formation of all possible products of the reaction. Unimolecular rate constants are computed by RRKM theory. VRC-TST is used to compute the sum of quantum states for internal degrees of freedom of loose transition states. The present calculations reveal that the product HCCCCH + H (P8) is the dominant product over the whole pressure and temperature range considered in the present study. Nonetheless, at low temperatures and high pressures other intermediate products especially HCC(H)CCH and H_2CCCCH become significant. The overall computed rate constants are nearly constant over the temperature range 100-500 K and slightly increase at higher temperatures.

Keywords:- C_2H, C_2H_{2s}

INTRODUCTION

The kinetics and mechanism of the reaction between ethynyl radical (C_2H) and acetylene (C_2H_2) have received considerable scrutiny due to its importance in combustion [1-8] and interstellar chemistry [9-11]. In hydrocarbon flames, the C_2H + C_2H_2 reaction is thought to be a key reaction for the subsequent formation of polyacetylenes ($C_{2n}H_2$), polycyclic aromatic hydrocarbons and soot [1-8]. In the initial stages of soot formation in hydrocarbon flames, more than 50% of the primary fuel is believed to pass via the formation of diacetylene (C_4H_2), the main product of the C_2H + C_2H_2 reaction [2,7]. The title reaction is an important neutral-neutral condensation process in interstellar space and planetary atmospheres leading to form more complex species [9-10].

To date, many researchers have used different apparatus to measure the pressure and temperature dependence of the kinetic parameters of the $C_2H + C_2H_2$ reaction [9-24]. A synopsis of these measured kinetic parameters is provided in Table 1. Although a temperature-independent value of about 1.5×10^{-10} cm^3 molecule^{-1} s^{-1} is determined by most of the research groups at temperatures around 298 K, higher values are reported by early measurements. The HCCCCH + H are known as the major product of the reaction. However, there are discordant data on the temperature dependence of the rate constants at lower and higher temperatures. There are reports in the literature on positive [15], and negative [21] and no temperature dependence [17] of the rate coefficients. In addition, no experimental and theoretical studies have been performed on the significance of other possible product channels of the title reaction[9].

Table 1. The Arrhenius Parameters ($k = AT^n e^{-Ea/RT}$) for the Title Reaction Reported by Various Laboratories

T (K)	A (cm^3 molecule^{-1} s^{-1})	n	E_a (kJ mol^{-1})	Ref.[a]
100-1500	4.63×10^{-12}	0.56	0.624	Present work
295-800	1.3×10^{-10}			Ceursters 2000 [24]
143-359	2.44×10^{-11}	1.8	-3.941	Opansky 1996 [22]
295-448	1.3×10^{-10}			van Look 1995 [21]
170-350	1.1×10^{-10}		-0.23	Pedersen 1993 [20]
295-854	1.6×10^{-10}			Farhat 1993 [19]
298-2177	1.50×10^{-10}			Koshi 1992 [18]
296-1475	3.02×10^{-10}		1.95	Shin 1991 [15]
298	1.51×10^{-10}			Stephens 1987 [16]
298	3.10×10^{-11}			Laufer 1979 [13]
320	4.98×10^{-11}			Lange 1975 [12]

[a]The values in the parentheses are the corresponding reference numbers.

Herbst and Woon [9] have used a simple approach for computing the rate coefficient for the formation of HCCCCH + H. They have employed the phase-space approach on the base of a long-range potential which is assumed to be the sum of dispersion and induction terms. Ceursters *et al.* [24] have also investigated the PES of the $C_2H + C_2H_2$ reaction. They have optimized the structures of the stationary points at the B3LYP/6- 311++G(d,p) level of theory and performed single-point calculations at the CCSD(T)/6-311++G(d,p) level. In this research, statistical rate theories are employed to compute the rate constants for all possible reaction channels. First, the potential energy surface (PES) of the $C_2H + C_2H_2$ reaction is explored to compute the structures and energies of the stationary points of the reaction. Next,

transition state theory (TST) and RRKM statistical rate theories are used to compute the rate coefficients for different product channels at different temperatures and pressures.

Electronic-Structure Calculations

In the present research work, some well-tested electronic structure calculation methods are employed to optimize geometries and evaluate the energies of the stationary points on the PES of the title reaction. The geometries of the minimum energy structures and saddle points are fully optimized by the M06-2X hybrid *meta* density functional theory (HMDFT) method [25] along with the MG3S basis set [26]. The performance of the M06-2X method, developed by Truhlar and coworkers, is illustrated for representative databases containing energetic data, bond lengths, vibrational frequencies and vibrational zero point energies [25]. More accurate energies are obtained by single-point energy calculations at the unrestricted coupled cluster method with single, double and noniterative triple excitations UCCSD(T) [27] in combination with the standard AugH-cc-pVTZ+2df basis set [28]. In the latter basis set, the augmented correlation-consistent polarized triple-ζ basis set Aug-cc-pVTZ [29] is extended by adding high exponent d- and f-type basis functions so that inner- shell correlation effects are more correctly described. All electrons are included in the correlation calculations. In addition, spin-restricted open-shell calculations at the ROCCSD(T)/AugH-cc-pVTZ+2df are also carried out.

RESULTS AND DISCUSSION

As aforementioned, Ceursters et al. [24] have also explored the PES of the $C_2H + C_2H_2$ reaction at the CCSD(T)/6-311++G(d,p) level of theory. In the present study, higher levels of theory are employed to optimize the structures of the intermediates, transition states and products of the reaction and calculate their relative energies. On the basis of the geometries optimized at the M06-2X/MG3S level of theory, the mechanism of the reaction C_2H radical and acetylene can be demonstrated by Scheme 1. The z-matrices for reactants, intermediates and transition states arising from the $C_2H + C_2H_2$ reaction are given in Supplemental Information. The relative energies of the stationary points located on the doublet potential energy surface of the $C_2H + C_2H_2$ reaction computed at M06- 2X/MG3S, CBS-Q, G4, UCCSD(T)/Aug-cc-pVTZ+2df and

ROCCSD(T)/Aug-cc-pVTZ+2df levels of theory are listed in Table 2. As it is seen, the computed energies are slightly dependent on the employed quantum-chemical methods. In addition, due to the presence of two multiple bond systems, the wave functions are spin-contaminated with large expectation values for $(S^2) > 1.0$. The latter points about the title reaction have also been mentioned by Ceursters *et al.* [24]. A recent research shows that one should be very careful using spin-unrestricted methods with high values of $<S^2>$ [52]. Blanquart [31] has obtained a good set of estimates for the enthalpies of formation for some critical polycyclic aromatic hydrocarbon radicals using spin-restricted open- shell ROCCSD(T) calculations [30].

The reaction proceeds via the addition of each carbon atom of C_2H radical to either of the carbon atom of the triple bond of $HC{\equiv}CH$, leading to the product P2 or the intermediate INT3. According to the energies computed at the ROCCSD(T)/Augh-cc-pVTZ+2df level, the barrier height for the formation of P2 *via* TS1/2 is 18.7 kJ mol^{-1}. P2, in which C_2H is attached via its central carbon atom to the carbon atom of acetylene, is 70.4 kJ mol^{-1} more stable than the reactants. As mentioned in the previous section, the formation of INT3 is a barrierless process; *i.e.*, no well- distinguished saddle-point is formed during the process. The energy of INT3 is 264.3 kJ mol^{-1} lower than the reactants. Next, INT3 isomerizes to give the three member ring intermediate INT4 by passing through the transition state TS3/4. The barrier height for this process is 108.3 kJ mol^{-1} and the energy of INT4 is 87.0 kJ mol^{-1} higher than INT3. INT4 may in turn undergo an isomerization reaction to give four-membered ring P5. The barrier height of the latter isomerization reaction from INT4 is 139.9 kJ mol^{-1} and energy of P5 is 18.1 kJ mol^{-1} higher than that for INT4. INT3 may be also converted to P2 *via* TS3/2 with the barrier height of 183.6 J mol^{-1}. INT3 passes through the transition state TS3/7 with the barrier height of 171.7 kJ mol^{-1} to give the intermediate INT7. The energy of INT7 is 55.1 kJ mol^{-1} lower than INT3. INT7 is decomposed to yield HCCCCH + H (P8) via the transition state TS7/8 with energy of 191.7 kJ mol^{-1} higher than INT7. The intermediate INT3 can be also directly decomposed to P8 through the transition state TS3/8. The barrier height of this process is 154.5 kJ mol^{-1}.The harmonic vibrational frequencies and the principle moments of inertia of the reactants, intermediates and transition states used in kinetic calculations, calculated at the M06-2X/MG3S level of theory, are provided in Table 2 in Supplemental Information.

Table 2. The Relative Energies of the Stationary Points for the $C_2H + C_2H_2$ Reaction Computed at some Levels of Theory in kJ mol^{-1}. All Values are Corrected for Zero Point Energies

	CBS-QB3	G4	M06-2X[a]	UCCSD(T)[b]	ROCCSD(T)[b]	CCSD(T)[c]
P2	-51.1	-48.2	-53.6	-68.4	-70.4	-55
INT3	-246.5	-243.6	-251.8	-260.2	-264.3	-239
INT4	-157.6	-155.8	-184.6	-177.5	-177.3	-147
P5	-139.7	-137.2	-144.7	-154.2	-159.2	-130
INT7	-299.4	-289.0	-304.8	-312.1	-319.4	-295
P8	-117.4	-113.4	-123.5	-140.3	-140.3	-110
TS1/2	35.9	40.4	26.6	23.3	18.7	32
TS3/4	-137.9	-132.2	-144.1	-152.3	156.0	-123
TS3/2	-53.1		-69.1	-73.1	-80.7	
TS3/7			-80.1	-90.7	-92.6	-65
TS3/8	-91.8	-86.9	-88.8	-104.5	-109.8	-73
TS4/5	-12.3	-11.3	-26.5	-26.0	-37.4	
TS7/8	-106.2	-103.5	-107.9	-122.4	-127.7	-98

[a]The basis set MG3S is used. [b]The basis set AugH-cc-pVTZ+2df is used. [c]The basis set 6-311++G** is used (Ref. [24]).

As a consequence, the product P8 is dominant channel and nearly pressure independent. As temperature decreases, the formation of the intermediates INT3, INT4, INT5 and INT7 become important. The reason is that at lower temperatures, the intermediates with lower internal energies are formed and consequently the deactivation processes become important. It should be mentioned that the rate constants for the formation of chemically-activated intermediates are pressure-dependent. This is a reasonable result because the rate constants for the de-activation of the active intermediates depend on the pressure of the system.

The computed overall rate coefficients are pressure independent since the rate coefficients for the dominant channel (channel P8) does not depend on the pressure. The present overall computed rate constants are nearly constant over the temperature range 100-500 K and slightly increase at higher temperatures. The present theoretical results are in accordance with most of the experimental data. The empirical data of Refs. [12] and [13] are slightly lower than the other experimental data and present computed rate coefficients. The overall computed rate constants obtained in the present work are fitted to an extended Arrhenius equation. The values of parameters are reported in Table 1. In addition, the numerical calculated values of the rate coefficients along with the corresponding experimental values for some selected temperatures are provided in the Supplemental Information. As mentioned in the Introduction section, Herbst and Woon [9] have used a phase-space approach to compute the overall rate coefficient (being considered the HCCCCH + H as the only product of the reaction). Their computed rate coefficients are about a factor of 4 greater than the largest experimental values. The computed rate coefficients for the formation of various products as a function of temperature at the pressures 1, 100 and 760 Torr. It is seen that the product channel P8 is the dominant product channel at all temperatures and pressures. However, as pressure increases, the rate constants for the formation of all intermediates increase due to increasing the rate of collisional deactivation processes. In the interstellar spaces where the temperature is very low, it is predicted that the intermediates such as HCC(H)CCH and H_2CCCCH become important.

CONCLUSIONS

In this research, the kinetics and mechanism of the $C_2H + C_2H_2$ reaction is investigated theoretically. High level electronic structure theories are employed to locate the stationary points on the potential energy surface of the reaction and compute their rovibrational properties and energies. Statistical rate theories are employed to compute the rate constants of various possible products as a function of temperature and pressure.

References :-

1. Bonne, U.; Homann, K. H.; Wagner, H. G., Carbon formation in premixed flames. *Symp. (Int.) Combust. [Proc.],* **1965**, *10*, 503-512, DOI: 10.1016/S0082- 0784(65)80197-7.

2. Warnatz, J., The mechanism of high temperature combustion of propane and butane. *Combust. Sci. Technol.,* **1983**, *34*, 177-200, DOI: 10.1080/ 00102208308923692.

3. Bittner, J. D.; Howard, J. B., Mechanism of hydrocarbon decay in fuel-rich secondary reaction zones. *Symp. (Int.) Combust. [Proc.],* **1982**, *19*, 211- 221, DOI: 10.1016/S0082-0784(82)80191-4.

4. Frenklach, M.; Wang, H., Detailed modeling of soot particle nucleation and growth. *Symp. (Int.) Combust. [Proc.],* **1990**, *23*, 1559-1566, DOI: 10.1016/S0082- 0784(06)80426-1.

5. Lindstedt, R. P.; Skevis, G., Chemistry of acetylene flames, *Combust. Sci. Technol.,* **1997**, *125*, 73-137, DOI: 10.1080/00102209708935656.

6. Doute, C.; Delfau, J. -L.; Vovelle, C., Reaction mechanism for arornatics formation in a low pressure, premixed acetylene-oxygene/argon flame. *Combust. Sci. Technol.,* **1994**, *103*, 153-173, DOI: 10.1080/ 00102209408907692.

7. Warnatz, J., Hydrocarbon oxidation at high temperatures. *Ber. Bunsenges. Phys. Chem.,* **1983**, *87*, 1008-1022, DOI: 10.1002/bbpc.19830871111.

8. Bockhorn, H.; Fetting, F.; Wenz, H. W., Investigation of the formation of high molecular hydrocarbons and soot in premixed hydrocarbon-oxygen flames. *Ber. Bunsenges. Phys. Chem.,* **1983**, *87*, 1067-1073, DOI: 10.1002/bbpc.19830871121.

9. Herbst, E.; Woon, D. E., The rate of the reaction between C_2H and C_2H_2 at interstellar temperatures. *Astrophys. J.,* **1997**, *489*, DOI: 109-112, 10.1086/ 304786.

10. Chastaing, D.; James, P. L.; Sims, I. R.; Smith, I. W. M., Neutral-neutral reactions at the temperatures of interstellar clouds Rate coefficients for reactions of C2H radicals with O_2, C_2H_2, C_2H_4 and C_3H_6 down to 15 K. Faraday Discuss. **1998**, *109*, 165-181, DOI: 10.1039/A800495A.

11.]Kovaćs, T.; Blitz, M. A.; Seakins, P. W., H atom yields from the photolysis of acetylene and from the reaction of C_2H with H_2, C_2H_2 and C_2H_4. *J. Phys. Chem. A,* **2010**, *114*, 4735-4741, DOI: 10.1021/ jp908285t.

12. Lange, W.; Wagner, H. G., Massenspektrometrische untersuchungen über erzeugung und reaktionen von C_2H-radikalen. *Ber. Bunsenges. Phys. Chem.,* **1975**, *79*, 165-170, DOI: 10.1002/bbpc.19750790210 .

13. Laufer, A. H.; Bass, A. M., Photochemistry of acetylene. bimolecular rate constant for the formation of butadiyne and reactions of ethynyl radicals. *J. Phys. Chem.,* **1979**, *83*, 310-313, DOI: 10.1021/ j100466a002.

14. Okabe, H., Photochemistry of acetylene at 1470 Å. *J. Chem. Phys.,* **1981**, *75*, 2772-2778, DOI: 10.1063/ 1.442348.

15. Shin, K. S.; Michael, J. V., Rate constants (296-1700K) for the reactions $C_2H + C_2H_2 = C_4H_2 + H$ and $C_2D + C_2D_2 = C_4D_2 + D$. *J. Phys. Chem.,* **1991**, *95*, 5864- 5869, DOI: 10.1021/j100168a029.

16. Stephens, J. W.; Hall, J. L.; Solka, H.; Yan, W.-B.; Curl, R. F.; Glass, G. P., Rate constant measurements of reactions of C_2H with H_2, O_2, C_2H_2, and NO using color center laser kinetic spectroscopy. *J. Phys. Chem.,* **1987**, *91*, 5740-5743, DOI: 10.1021/ j100306a044.

17. Koshi, M.; Fukuda, K.; Kamiya, K.; Matsui, H., Temperature dependence of the rate constants for the reactions of ethynyl radical with acetylene, hydrogen, and deuterium. *J. Phys. Chem.,* **1992**, *96*, 9839-9843, DOI: 10.1021/j100203a048.

18. Koshi, M.; Nishida, N.; Matsui, H., Kinetics of the reactions of C_2H with C_2H_2, H_2 and D_2. *J. Phys. Chem.,* **1992**, *96*, 5875-5880, DOI: 10.1021/ j100193a043.

19. Farhat, S. K.; Morter, C. L.; Glass, G. P., Temperature dependence of the rate of reaction of C_2H with

H_2. *J. Phys. Chem.,* **1993**, *97*, DOI: 12789-12792, 10.1021/ j100151a026.

20. Pedersen, J. O. P.; Opansky, B. J.; Leone, S.R., Laboratory studies of low-temperature reactions of C_2H with C_2H_2 and implications for atmospheric models of titan. *J. Phys. Chem.,* **1993**, *97*, 6822-6829.

21. Van Look, H.; Peeters, J., Rate coefficients of the reactions of C_2H with O_2, C_2H_2, and H_2O between 295 and 450 K. *J. Phys. Chem.,* **1995**, *99*, 16284-16289, DOI: 10.1021/j100044a013.

22. Opansky, B. J.; Leone, S. R., Low-temperature rate coefficients of C_2H with CH_4 and CD_4 from 154 to 359 K. *J. Phys. Chem.,* **1996**, *100*, 4888-4892, DOI: 10.1021/jp9532677.

23. Brachhold, H.; Alkemade, U.; Homann, K. H., Reactions of ethynyl radicals with alkynes in the system sodium vapour/ethynylbromide/alkyne. *Ber. Bunsenges. Phys. Chem.,* **1988**, *92*, 916-924, DOI: 10.1002/bbpc.198800220.

24. Ceursters, B.; Nguyen, H. M. T.; Peeters, *J.; Nguyen, M. T., Chem. Phys.,* **2000**, *262*, 243-252, DOI: 10.1016/S0301-0104(00)00337-2.

25. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functional. *Theory Chem. Acc.,* **2008**, *120*, 215-241, DOI: 10.1007/s00214-007- 0310-x.

26. Lynch, B. J.; Zhao, Y.; Truhlar, D. G., Effectiveness of diffuse basis functions for calculating relative energies by density functional theory. *J. Phys. Chem. A,* **2003**, *107*, 1384-1388, DOI: 10.1021/jp021590l.

27. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head- Gordon, M., A fifth-order perturbation comparison of electron correlation theories. *Chem. Phys. Lett.,* **1989**, *157*, 479-483, DOI: 10.1016/S0009-2614(89)87395-6.

28. Martin, J. M. L.; de Oliveira, G., Towards standard methods for benchmark quality *ab initio* thermochemistry-W1 and W2 theory. *J. Chem. Phys.,* **1999**, *111*, 1843-1856, DOI: 10.1063/1.479454.

29. Kendall, R. A.; Dunning, T. H.; Harrison, R. J., Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions, Electron affinities of the first-row atoms revisited. *J. Chem. Phys.,* **1992**, *96*, 6796-6806, DOI: 10.1063/1.462569.

30. Montgomery Jr., J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A., A complete basis set model chemistry. VI. Use of density functional geometries and frequencies. *J. Chem. Phys.,* **1999**, *110*, 2822-2827, DOI: 10.1063/1.477924.

31. Blanquart, G., Effects of spin contamination on estimating bond dissociation energies of polycyclic aromatic hydrocarbons. *Inter. J. Quantum Chemistry* **2015**, *115*, 796-801, DOI: 10.1002/qua.24904.