Theoretical Studies on the Potential Energy Surfaces of N_8 Clusters

Qian Shu Li*,†,‡ **and Li Jie Wang**†

School of Chemical Engineering and Materials Science, Beijing Institute of Technology, Beijing 100081, China, The National Key Laboratory of Theoretical and Computational, Chemistry of Jilin University, Changchun 130023, China

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The potential energy surfaces for the synthesis and decomposition reaction of $N_8(C_S) \rightarrow N_5^+ + N_3^-$ and isomerization reaction of $N_8(C_S)$ to $N_8(C_{2h})$ were investigated by density functional theory (DFT). The species involved were fully optimized using four DFT methods. Relative energies were further calculated at the QCISD/6-311+G*//B3LYP/6-311+G* level. The barrier heights of $N_8(C_S) \rightarrow N_5^+ + N_3^-$ in forward and reverse directions were predicted to be 23.4 and 2.0 kcal/mol, respectively. Rate constants for the dissociation and synthesis pathways of $N_8(C_S)$ were found by use of variational transition state theory. The barrier height for the isomerization reaction of $N_8(C_S)$ to $N_8(C_{2h})$ was predicted to be 4.0 kcal/mol at the QCISD/6-311+G*//B3LYP/6-311+G* level.

Introduction

The great interest in carbon clusters has naturally raised the question of whether other important cluster species have been overlooked. Are there any stable molecules made of pure nitrogen? Many stable structures have been predicted theoretically for all-nitrogen clusters, but only a few have been prepared. In 1998 Christe et al.[1] synthesized the AsF_6^- salt of N_5^+ by reacting $N_2F^+AsF_6^-$ with HN_3 in anhydrous hydrogen fluoride at −78 °C. Prior to this successful experimental synthesis, only molecular nitrogen, isolated in 1772, and the azide ion, first synthesized in 1890, had ever been isolated, although a few other species have been seen fleetingly in gas-phase chemistry. Nitrogen clusters are of significant interest as high-energy density materials (HEDMs) for propulsion and explosive applications. The critical properties for effective HEDM molecules are high dissociation barrier and facile syntheses.

Xu et al.[2] investigated the potential energy surface (PES) of the $N_2F^+ + HN_3 \rightarrow N_5^+ + HF$ reaction in theory, and the result of prediction is in agreement with that of experiment,[1] which suggests the possible reaction pathway $N_5^+ + N_3^- \rightarrow N_8$. Our goal in this work was to study this synthetic pathway for N_8 clusters in theory in order to provide information for experimental synthesis of this possible HEDM molecule. Many stable structures of N_8 isomers have been predicted theoretically,[3−15] but none of them have been synthesized before now. Leininger et al.[10] have studied three isomers of N_8 (an octaazacubane structure, a D_{2h} structure analogous to cyclooctatetraene, and a planar bicyclic form analogous to pentalene). The geometries were optimized with Hartree−Fock self-consistent-field (SCF), Møller−Plesset perturbation theory (MP2), single and double excitation configuration interaction (CISD), and coupled-cluster method (CCSD) using a DZP basis set. Glukhovtsev[6] and Wang[16] predicted the structures of N_8 isomers, with O_h, D_{2h}, D_{2d}, C_S, C_{2h}, and C_{2v} symmetries. Bartlett et al.[4] discussed nitrogen clusters and calculated cubic N_8 clusters with SCF, coupled cluster (CC), and MP2 methods. From symmetry arguments, they deduced that N_8 should have a significant barrier to decompose. Their SCF results agree with those of Engelke.[11] Gagliardi[17] et al. have studied the PES of N_8 isomers. Gagliardi et al. investigated the stability of ten N_8 isomers and the possible dissociation of N_8 to four N_2.[13,14] To understand the dissociation channels of N_8, some results have been presented by studies of the isomerization reaction from the high-energy azacubane structure to the more stable azapentalene structure.[9] This reaction may occur via a series of intermediate metastable structures with moderately low barriers (10−20 kcal/mol). Five local minima on the potential energy surface have been found, and the transition states between two continuous minima have been determined.

In our present work, the PES and rate constants of the $N_8(C_S) \rightarrow N_5^+(C_{2v}) + N_3^-\ (D_{\infty h})$ reaction and the isomerization reaction pathway of $N_8(C_S)$ to $N_8(C_{2h})$ were studied. The structures of the stationary points along the minimum energy path (MEP) were optimized. The linear forms may be the intermediates in the decomposition or synthesis of the probably more kinetically stable (and higher energy) polycyclic forms containing the same number of nitrogen atoms. Therefore, studies of the potential energy surface and the isomerization reaction of the linear molecules would provide a theoretical foundation for synthesizing more stable N_8 clusters as HEDMs in the future.

Computational Method

The geometries of N_8 isomers and the transition states involved in the reactions were optimized using density functional theory (DFT) methods. The functionals used in the present work comprise the set of combinations of Becke's 1988 and three-parameter exchange functionals with the nonlocal Lee, Yang, Parr, and Perdew−Wang 1991 correlation functionals,[18,19] hereafter denoted as BLYP, B3LYP, BPW91, and B3PW91. The 6-31G* is a standard split-valence double-ζ polarization basis set, while the 6-311+G* is a split-valence triple-ζ polarization basis set augmented with diffuse functions,[20] both

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* Corresponding author. FAX: +86-10-6891-2665. Telephone: +86-10-6891-2665. E-mail: qsli@mh.bit.edu.cn.

† Beijing Institute of Technology.

‡ The National Key Laboratory of Theoretical and Computational Chemistry of Jilin University.

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TABLE 1: Total Energies (in hartrees) of Species; ZPE (in kcal/mol) in Parentheses

	6-31G*				6-311+G*
	B3LYP	B3PW91	BLYP	BPW91	B3LYP
$N_5^+(D_{5h})$	−273.282 99 (12.8)	−273.172 92 (13.0)	−273.271 59 (12.0)	−273.293 81 (12.4)	−273.356 38 (12.7)
$N_3^-(D_{\infty h})$	−164.213 09 (7.0)	−164.149 50 (7.1)	−164.195 37 (6.6)	−164.218 24 (6.7)	−164.285 58 (6.7)
Complex(C_S)	−437.746 59 (20.5)	−437.571 10 (20.9)	−437.725 62 (19.0)	−437.767 60 (19.7)	−437.870 94 (20.3)
TS(C_S)	−437.743 86 (20.3)	−437.568 34 (20.7)	−437.722 48 (18.8)	−437.764 55 (19.5)	−437.867 08 (20.1)
TS1(C_1)	−437.763 89 (20.8)	−437.591 30 (21.2)	−437.733 31 (19.4)	−437.779 46 (19.9)	−437.887 49 (20.7)
$N_8(C_S)$	−437.773 02 (21.0)	−437.600 87 (21.4)	−437.742 27 (19.5)	−437.789 15 (20.1)	−437.896 23 (20.8)
$N_8(C_{2h})$	−437.777 75 (21.2)	−437.605 56 (21.6)	−437.746 49 (19.8)	−437.793 33 (20.3)	−437.902 17 (21.1)

TABLE 2: Relative Energies (kcal/mol) of Species

	6-31G*				6-311+G*	
	B3LYP	B3PW91	BLYP	BPW91	B3LYP	QCISD/6-311+G*//B3LYP/6-311+G*
$N_5^+ + N_3^-$	150.2	155.2	161.9	159.9	143.0	136.0
Complex(C_S)	0.0	0.0	0.0	0.0	0.0	0.0
TS(C_S)	1.5	1.5	1.8	1.7	2.2	2.0
$N_8(C_S)$	−16.1	−18.2	−9.9	−13.1	−15.4	−21.4
TS1(C_1)	−10.6	−12.4	−4.4	−7.2	−10.0	−17.4
$N_8(C_{2h})$	−18.9	−17.2	−12.3	−15.5	−18.8	−24.9

of which were introduced by Pople and co-workers. The relative energies were further calculated using quadratic configuration interaction calculation, including single and double substitution[21] (QCISD) methods at the QCISD/6-311+G*//B3LYP/6-311+G* levels. All calculations were carried out with the Gaussian 94 program package[22] on a SGI Origin 2000 server. To characterize the nature of the stationary points and determine the zero-point-energy (ZPE) corrections, harmonic vibrational frequencies were also calculated at the levels of theory mentioned above. Stationary points were identified as either local minima or transition states. To confirm that a given transition state connects reactants and products, intrinsic reaction coordinate (IRC)[23,24] calculations were performed at the above levels with a gradient step size of 0.1 (amu)$^{1/2}$ bohr.

In this work, we also calculated the rate constants for this reaction with variational transition state theory (VTST) using the tunneling effect corrections of Wigner[25] (semiclassical transmission coefficient k^W) and MEPSAG[26] (semiclassical adiabatic ground-state method along MEP) methods. The POLYRATE 8.2 program[27] was employed to calculate the theoretical rate constants using VTST theory and the above two methods (denoted in this paper as TST, TST/w, and TST/MEPSAG, respectively). The forward and reverse reaction rate constants were obtained by the variational transition state theory at the B3LYP/6-311+G* level of theory for temperature ranges appropriate to those barriers.

Results and Discussion

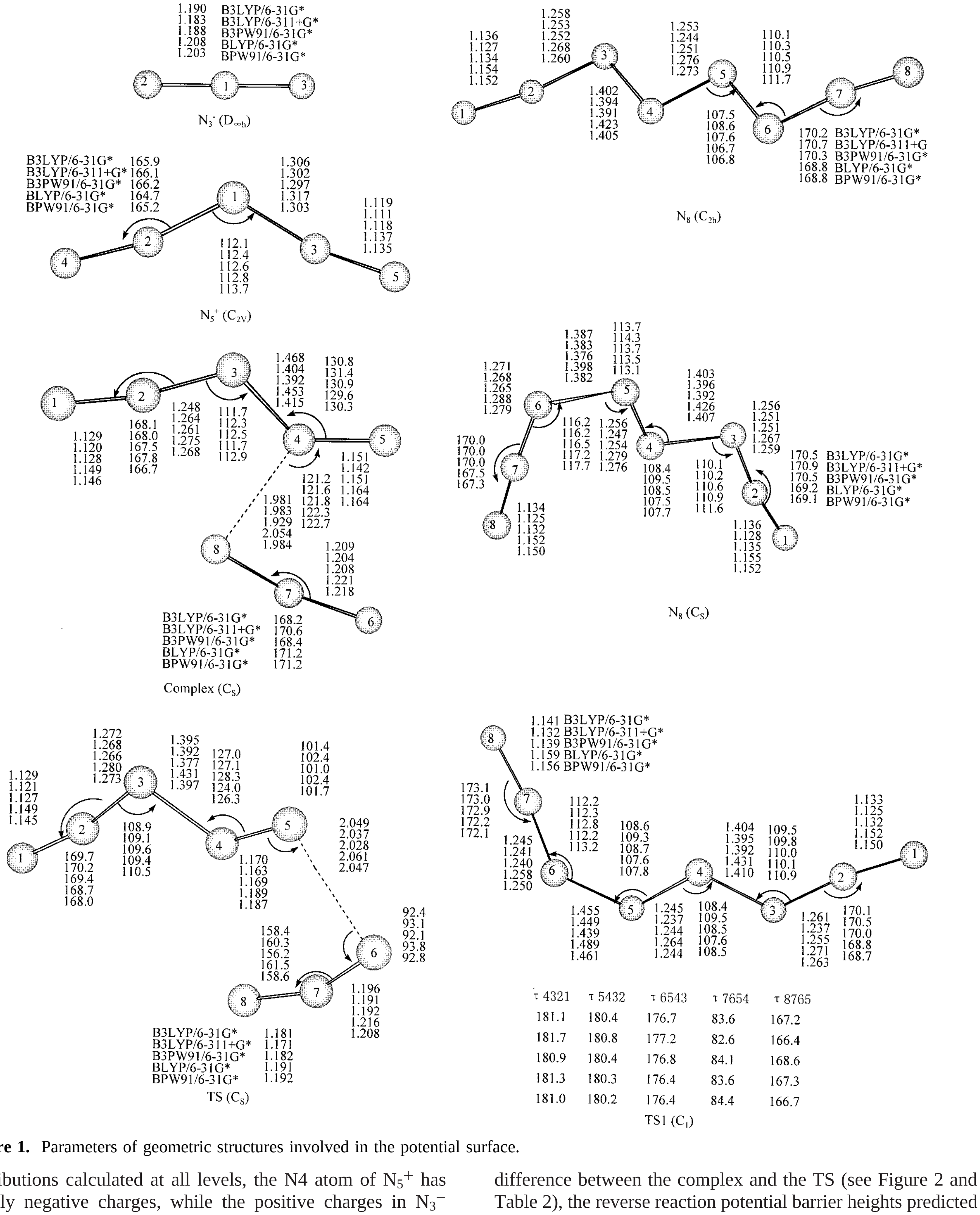
The optimized structures of the species are presented in Figure 1. Total energy and ZPE are listed in Table 1. The relative energies are presented in Table 2.

1. Geometric Structures of the N_8 System. The geometric structures of N_8 (C_S and C_{2h}), intermediate (Complex), transition states (TS and TS1), N_5^+, and N_3^- are all open-chain structures (see Figure 1). The results were calculated using four DFT methods, but only B3LYP results were computed using two types of basis sets (6-31G* and 6-311+G*). Therefore, in the following discussions, we will mainly use the B3LYP/6-311+G* results unless otherwise indicated. As can be seen in the Figure 1, the N_5^+ cation has C_{2v} symmetry, while N_3^- is a linear molecule. In the structure of the complex, the bond of N4−N8 forms by the N4 atom connecting the N8 atom with charge−charge force; the other bond lengths lie between single and triple bond lengths. N_8 isomers have C_S and C_{2h} symmetry. The structure TS is the transition state of the $N_8(C_S) \rightarrow N_5^+(C_{2v}) + N_3^-(D_{\infty h})$ reaction with C_S symmetry.

2. PES of the Isomerization Reaction. The $N_8(C_{2h})$ isomer is an open-chain structure. As shown in Figure 1, one kind of bond length in structure C_{2h}, 1.394 Å (B3LYP/6-311+G*), lies between single and double bond lengths. Another kind of bond length is near the experimental double bond length 1.252 Å of N_2H_2. The structure TS1, with C_1 symmetry, is the transition state of the isomerization reaction $N_8(C_S) \rightarrow N_8(C_{2h})$. The bond lengths and angles of the structure TS1 are near those of $N_8(C_{2h})$ except in the dihedral angle of N8−N7−N6−N5. During the process of changing from $N_8(C_S)$ to $N_8(C_{2h})$, the barrier height with ZPE correction is 5.4 kcal/mol (B3LYP/6-311+G*). The pathway has been confirmed by the IRC calculation at the above levels (Figure 2).

3. PES of the Dissociation and Synthesis Reactions. For the $N_8(C_S) \rightarrow \mathrm{TS} \rightarrow \mathrm{Complex} \rightarrow N_5^+ + N_3^-$ process, in the forward direction, the starting point in the mechanism is $N_8(C_S)$. With the distance between N5 and N6 atoms lengthening, the structure transfers into an intermediate (Complex). The complex is a local minimum (see Figure 2) on the PES due to its all-real harmonic vibrational frequencies at all levels of theory. In the structure, the N4 atom of N_5^+ connects the N8 atom of N_3^- through long-range Coulomb induced force. Separation of the N5−N6 bond is longer than that in stable $N_8(C_S)$. The long distance between N5 and N6 atoms suggests that the charge attraction force between N5 and N6 is weakened. The bond length of N5−N6 changes obviously in the course of reaction, while those of the others change slightly. Thus, the bond of N5−N6 would break and $N_8(C_S)$ would dissociate into two species: $N_5^+ + N_3^-$. In the complex, the sum of charge from N1 to N5 is +0.23 (B3LYP/6-31G*), corresponding to that of product N_5^+, and that from N6 to N8 (product N_3^-) is −0.23, corresponding to that of product N_3^-. Therefore, we believe that N_8 dissociates into N_5^+ and N_3^-, and not into a pair of neutral radicals. The barrier at the level of QCISD/6-311+G*//B3LYP/6-311+G* is 23.4 kcal/mol. Therefore, the decomposition of the N_8 cluster is an endothermic reaction. All of our calculations predict the heat of the $N_8(C_S) \rightarrow \mathrm{Complex}(C_S)$ reaction to be in the range of 9.9−18.2 kcal/mol, and the heat of the whole reaction is 157.4 kcal/mol at the QCISD/6-311+G*//B3LYP/6-311+G* level.

In the reverse direction, the starting point in the mechanism is the formation of an ion−ion complex. According to the charge



τ 4321	τ 5432	τ 6543	τ 7654	τ 8765
181.1	180.4	176.7	83.6	167.2
181.7	180.8	177.2	82.6	166.4
180.9	180.4	176.8	84.1	168.6
181.3	180.3	176.4	83.6	167.3
181.0	180.2	176.4	84.4	166.7

TS1 (C_1)

Figure 1. Parameters of geometric structures involved in the potential surface.

distributions calculated at all levels, the N4 atom of N_5^+ has mostly negative charges, while the positive charges in N_3^- mainly concentrate on the N8 atom. When the two ions attack each other, the N4 atom mainly attacks the N8 atom through long-range Coulomb induced force. Therefore, the complex can be formed without any activation energy barrier. As shown in Figure 2 and Table 2, the complex is significantly more stable than the reactants ($N_5^+ + N_3^-$) in energy. The structures along the PES of the reverse direction change with the bond distance of N4−N8 increasing and that of N6−N5 decreasing. Finally, the bond N5−N6 forms by charge−charge force; then the complex transfers into N_8 through TS. On the basis of the energy difference between the complex and the TS (see Figure 2 and Table 2), the reverse reaction potential barrier heights predicted by all above levels of theory are in the range of 1.5−2.0 kcal/mol. The lower barrier height implies that the reverse direction reaction happens easily.

To verify that the transition state really connects the complex and N_8(*CS*), IRC calculations were also performed beginning with each corresponding transition state at the levels of B3LYP/6-31G* and B3LYP/6-311+G*, respectively. The geometries of the two species obtained from these IRC calculations are very close to those from the geometry optimization calculations.

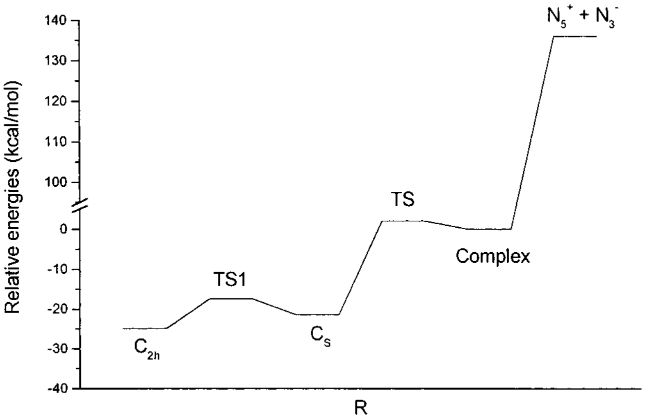


Figure 2. Potential surface of N_8 system at the QCISD/6-311+G*//B3LYP/6-311+G* level.

TABLE 3: Forward Reaction Rate Constants ($cm^3\ mol^{-1}\ s^{-1}$) for the $N_8(C_S) \rightarrow$ Complex(C_S) Reaction

T (K)	TST	TST/W	TST/MEPSAG
200.0	8.7424E−07	9.0674E−07	9.0356E−07
220.0	4.4351E−05	4.5714E−05	4.5576E−05
260.0	1.8868E−02	1.9283E−02	1.9239E−02
298.0	1.3311E+00	1.3533E+00	1.3509E+00
350.0	1.0192E+02	1.0315E+02	1.0301E+02
380.0	7.2866E+02	7.3616E+02	7.3531E+02
400.0	2.2984E+03	2.3198E+03	2.3174E+03
450.0	2.6070E+04	2.6262E+04	2.6240E+04
500.0	1.8254E+05	1.8363E+05	1.8350E+05
600.0	3.4005E+06	3.4145E+06	3.4129E+06

TABLE 4: Reverse Reaction Rate Constants ($cm^3\ mol^{-1}\ s^{-1}$) for the $N_8(C_S) \rightarrow$ Complex(C_S) Reaction

T (K)	TST	TST/W	TST/MEPSAG
30.0	2.1846E−03	5.7939E−03	9.8826E+00
50.0	1.8563E+03	2.9604E+03	3.3749E+03
60.0	5.6581E+04	7.9951E+04	8.3778E+04
80.0	4.0391E+06	4.9775E+06	4.9977E+06
100.0	5.2162E+07	5.9918E+07	5.9661E+07
200.0	8.6839E+09	9.0067E+09	8.9751E+09
220.0	1.3810E+10	1.4235E+10	1.4191E+10
298.0	4.6259E+10	4.7034E+10	4.6949E+10
310.0	5.2746E+10	5.3562E+10	5.3472E+10

Therefore, the synthesis reaction of $N_8(C_S)$ cluster by N_5^+ and N_3^- is an exothermic reaction. All of our calculations predict the exothermic heat of the whole reaction is 157.4 kcal/mol.

4. Rate Constants for the $N_8(C_S) \rightarrow$ Complex(C_S) Reaction. For the purpose of comparing the rate constants of the $N_8(C_S) \rightarrow$ Complex(C_S) reaction, the calculations of TST, TST/W, and TST/MEPSAG are performed to obtain the forward and reverse reaction rate constants in the temperature ranges from 200 to 600 K and from 30 to 310 K. Since the reaction from $N_8(C_S)$ to Complex is endothermic with a higher barrier, while the reverse reaction from Complex to $N_8(C_S)$ is exothermic with lower barrier, clearly the ideal reaction conditions will vary considerably. Therefore, we determined these rate constants using a higher temperature range (200−600 K) for the forward reaction and a lower temperature range (30−310 K) for the reverse reaction. The rate constants are shown in Tables 3 and 4. It can be seen that the forward does not occur appreciably while the reverse reaction happens readily at room temperature. The rate constants of TST are near those of TST/W and TST/MEPSAG, which implies that the variational effect for the calculation of the rate constants is small.

Summary

All our calculations on the potential energy surfaces and rate constants of synthesis and decomposition of N_8 clusters showed that the decomposition of $N_8(C_S)$ is an endothermic reaction and the synthesis of $N_8(C_S)$ by N_5^+ and N_3^- is an exothermic reaction. The only modestly high barrier of decomposition (21.4 kcal/mol) suggests that N_8's effectiveness as a HEDM molecule is marginal. The synthesis reaction, analogous to N_5^+, should be undertaken at a very low temperature. The heat of the $N_8(C_S) \rightarrow$ Complex(C_S) reaction is 19.4 kcal/mol, and the energy barrier height is 2.0 kcal/mol at the QCISD/6-311+G*//B3LYP/6-311+G* level of theory. The rate constants for the $N_8(C_S) \rightarrow$ Complex(C_S) reaction, obtained by the VTST theory at the B3LYP/6-311+G* level of theory, suggest a facile synthesis of N_8 that is largely resistant to dissociation. Therefore, this theoretical study of the PES provides a theoretical foundation for understanding the decomposition and synthesis mechanism of N_8, as well as suggesting the possibility of N_8 and other N_n clusters as HEDM molecules.

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References and Notes

(1) Christe, K. O.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *Angew. Chem.* **1999**, *38*, 2004.

(2) Xu, W. G.; Li, G. L.; Wang, L. J.; Li, S.; Li, Q. S. *Chem. Phys. Lett.* **1999**, *314*, 300.

(3) Trinquier, G.; Malrieu, J.; Daudey, J. *Chem. Phys. Lett.* **1981**, *80*, 552.

(4) Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1173.

(5) Gimarc, B. M.; Zhao, M. *Inorg. Chem.* **1996**, *35*, 3289.

(6) Glukhovtsev, M. N.; Jiao, H.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 7124.

(7) Leininger, M. L.; Sherrill, C. D.; Schaefer, H. F. *J. Phys. Chem.* **1995**, *99*, 9, 2324.

(8) Tian, A.; Ding, F.; Zhang, L.; Xie, Y.; Schaefer, H. F. *J. Phys. Chem. A* **1997**, *101*, 1946.

(9) Gagliardi, L.; Evangelisti, S.; Widmark, P.-O.; Roos, B. O. *Theor. Chem. Acc.* **1997**, *9*, 136.

(10) Leininger, M. L.; Sherrill, C. D.; Schaefer, H. F. *J. Phys. Chem.* **1995**, *99*, 2324.

(11) Engelke, R.; Stine, J. R. *J. Phys. Chem.* **1990**, *94*, 5689.

(12) Benjamin, M. G.; Zhao, M. *Inorg. Chem.* **1996**, *35*, 3289.

(13) Gagliardi, L.; Evangelisti, S.; Roos, B. O.; Widmark, P.-O. *J. Mol. Struct.* (*THEOCHEM*) **1998**, *428*, 1.

(14) Gagliardi, L. Evangelisti, S.; Bernhardsson, A.; Lindh, R.; Roos, B. O. *Int. J. Quantum Chem.* **2000**, *77*, 311.

(15) Li, J.; Liu, C-W.; Lu, J-X. *THEOCHEM* **1993**, *99*, 223.

(16) Wang, L. J. Xu, W. G.; Li, Q. S. *THEOCHEM* **2000**, *531*, 135−141.

(17) Chung, G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2000**, *104*, 5647.

(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(20) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(21) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(23) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(24) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(25) Dupuis M. J.; Lester, W. A., Jr.; Lengsfield, B. H.; Lui, B. *J. Chem. Phys.* **1983**, *79*, 6167.

(26) Truhlar, D. G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, *13*, 440.

(27) Chuang, Y.-Y.; Corchado, J. C.; Fast, P. L.; Villa, J.; Hu, W.-P.; Liu, Y.-P.; Lynch, G. C.; Jackels, C. F.; Nguyen, K. A.; Gu, M. Z.; Rossi, I.; Coitino, E. L.; Clyton, S.; Melissas, V. S.; Steckler, R.; Garrett, B. C.; Isaacson, A. D.; Truhlar, D. G. *POLYRATE*; University of Minnesota, 1998.