

Theoretically Catalytic Synthesis of 5-Nitro-1,2,4-Triazol-3-One in Inert Gas Clustered System (X_6 , $X = \text{He, Ne}$)

Min-Hsien Liu*, Ming-Yung Wu

Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology National Defense University, Taiwan, China
Email: minhsienliu@gmail.com

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ABSTRACT

Inert gas-clustered systems (X_n , $X = \text{He, Ne, Ar}$ and $n = 2 - 20$) were established in this study and their stability as a result of interparticulate interaction was examined. Ferric chloride and ferrous oxides were used as catalysts to promote reaction, and 5-nitro-1,2,4-triazol-3-one (NTO) was theoretically synthesized under an inert gas (X_6)-clustered environment in this study. The raw material, urea, initially underwent chlorination using chlorine as the reagent, followed by amination, formylation and nitration. Reaction routes closely related to the experimental processes were successfully constructed, and the corresponding energy barriers were estimated for each elementary reaction. The findings revealed that the average errors in the B3LYP/6-31G(d, p)-calculated geometry and vibrational frequency of NTO in an Ne_6 system relative to the observed values were 0.83% and 1.84%, respectively. The neon gas-clustered system achieved greater stabilization, which results from the difference in self-consistent field energy (E_{SCF}), than the corresponding stabilization acquired in a helium- or argon-based system. Ferric chloride serves as a good catalyst to reduce the energy barrier of the chlorination reaction, and ferrous oxide is suitable for catalyzing the amination, formylation and nitration reactions, although nitric acid is the better agent for nitration. The catalytic Ne_6 -clustered reaction system is suggested to be a more feasible pathway for the synthesis of NTO.

Keywords: NTO; Inert Gas Clustered System; Metal Catalyst; Formylation Reaction

1. Introduction

In synthesis chemistry, specific materials are obtained efficiently under certain conditions through a well-designed chemical reaction. The design of an optimum reaction, including the use of suitable reagents and the setting of the reaction conditions, is an important issue and is usually considered prior to performing experiments. Generally, the whole scheme of kinetic details is confined to the fast rate of the general reaction, which cannot be easily understood through experimental techniques. The adoption of theoretical calculation methods [1-9] has been proposed to overcome the shortage of experiments in recent decades. Based upon our experience in this area, computational effort has been devoted to the development of new high-energy-density materials (HEDM), TNAD and TNAZ derivatives, [10,11] and to the exploration of the kinetic reaction pathways of FOX-7 and TNT synthesis [12,13] in our lab. There remains the question of the reliability of the computational results. Basic geometric and vibrational analyses are required to compare the cal-

culated data with the observed values. Comparison of molecular geometries for a single molecule in the gaseous phase always shows apparent deviation from related X-ray analysis of molecules those with intermolecular interactions in condensed phase. Furthermore, interpretation and analysis of the accuracy of the theoretical frequencies should be performed in connection with gas-phase experimental results using a rare gas matrix [14-18]. The geometry and vibrational frequency apparently have a significant influence on the molecular thermodynamic properties and the reaction kinetics, and accordingly the phase environment has to be taken into consideration when performing calculations. It is said that short-lived, highly-reactive species such as radical ions and reaction intermediates may be observed using the matrix isolation technique and identified by spectroscopic means. [19,20] Molecular modeling in a rare gas-clustered system is regarded as being closely related to experiments using a gas matrix in the real gaseous world.

A promising material, 5-nitro-1,2,4-triazol-3-one (NTO), has emerged as a potential high-performance (e.g., cf. detonation velocity, detonation pressure) insensitive ex-

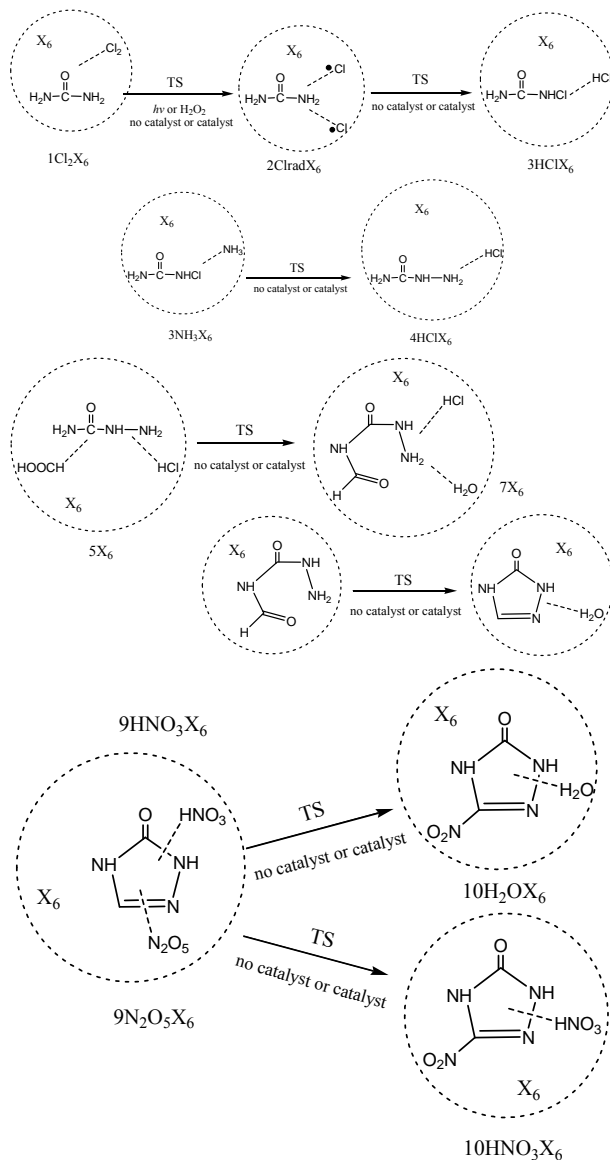
*Corresponding author.

plusive [21,22-26] that might endure a heavy mechanical and thermal impact, and this material is being explored as a substitute for RDX in munitions. NTO is easily prepared by the reaction of semicarbazide hydrochloride (SC) with formic acid followed by nitration with 70% nitric acid at 60°C [27]. There are many studies of NTO in the literature, including experiments that have been carried out to explore ways in which to improve the synthesis of the condensed phase of NTO [28-30], and some publications have discussed its thermal properties and decomposition kinetics [30-32]. Experimental and theoretical consideration of the structure of NTO and vibrational analysis [32-35] using quantum mechanical methods will provide more insight into the decomposition of NTO. In spite of theoretical aspects of chemical reactivity providing a broad overview of recent theoretical and computational advancements in the field of chemical reactivity [36-38], there exists little information regarding the application of theoretical techniques to simulate chemical reactions. This work is based on theory and refers to the related reaction mechanisms (Scheme 1) [27] in order to elucidate catalytic reaction routes for NTO synthesis in a special inert gas-clustered system. The reactivity of the reactants, which is generally inversely proportional to the molecular stability, indicates the rate at which a chemical substance tends to undergo a chemical reaction, was mainly concerned herein. Additionally, the integrated stabilization energy that arises from interparticle interaction in specific rare gas systems was examined and the related stabilization effect was inferred in order to identify the best gaseous reaction environment. In such stable systems, the proposed reaction profile included catalytic chlorination→amination→formylation→cyclocondensation→nitration in sequence using suitable reagents and catalysts. The comparable activation energies of each reaction stage were then used to identify favorable pathways to improve the synthesis of NTO.

2. Computations

2.1. Geometrical Optimization and Molecular Thermodynamic Energy

Electronic structure calculations have been performed with the Gaussian 98 program [39]. Full geometry optimizations were made for all the stationary points using the B3LYP [40] hybrid density functionals and the 6-31G(d, p) basis set. Restricted calculations were used for closed shell systems and unrestricted ones for open shell systems. Frequency calculations were carried out for all the stationary points at the corresponding level of theory. Local minima and transition states were identified by the number of imaginary frequencies (0 or 1, respectively). The B3LYP/6-31G(d, p) method was used to calculate



Scheme 1. Suggested reaction mechanisms of NTO synthesis in rare gas clustered system (X_6 , $X = \text{He, Ne}$).

the molecular energy (E_{SCF}). Molecular thermal enthalpy (H) and Gibbs energy (G) were obtained by adding thermal correction to the molecular energy.

2.2. Transition-States Modeling

The transition-state species were modeled using the B3LYP/6-31G(d, p) calculation method and were then identified using the QST3-type optimization procedure in the program. [41,42] Any pairs of equally-sized molecular systems (with the same numbers of C, H, O and N atoms) from the optimized products of the reaction species were selected, and the created input file, with two sets of relative atomic Cartesian coordinates, was included in the QST3 calculation. The activation energy for each

elementary reaction step was determined from the thermal enthalpy difference between a reactant and a transition complex.

3. Results and Discussion

3.1. Molecular Geometry and Energy

The B3LYP/6-31G(d, p)-modeled geometries of inert gas-clustered X_n ($X = \text{He, Ne, Ar}$, $n = 2 - 20$) indicated a shorter average interparticulae distance in the Ne system. (cf. 5.033 Å in Ne_6 , 5.458 Å in He_6 and 5.701 Å in Ar_6 ; **Figure 1**) Additionally, the stabilization energy, which results from the difference in self-consistent field energy between $E_{\text{SCF}}(X_n)$ and $nE_{\text{SCF}}(X)$, indicated the relative stability of the Ne-clustered system (**Figure 2** and **Table 1**). The geometry of NTONE_6 (**Scheme 2**) was then compared with the experimental values [33,34,43,44] (**Table 2**), and the results showed a 0.83% average relative error in bond length and a 1.84% average relative error in vibrational frequency, which revealed that B3LYP/6-31G (d, p) was an accurate method for further computational use.

The related geometries of all species, including the optimized reactants and products (all with positive frequencies) and transition complexes (one with an imaginary frequency), in a He_6 or Ne_6 gaseous environment indicated a weakly-bound molecular system (Figure in the

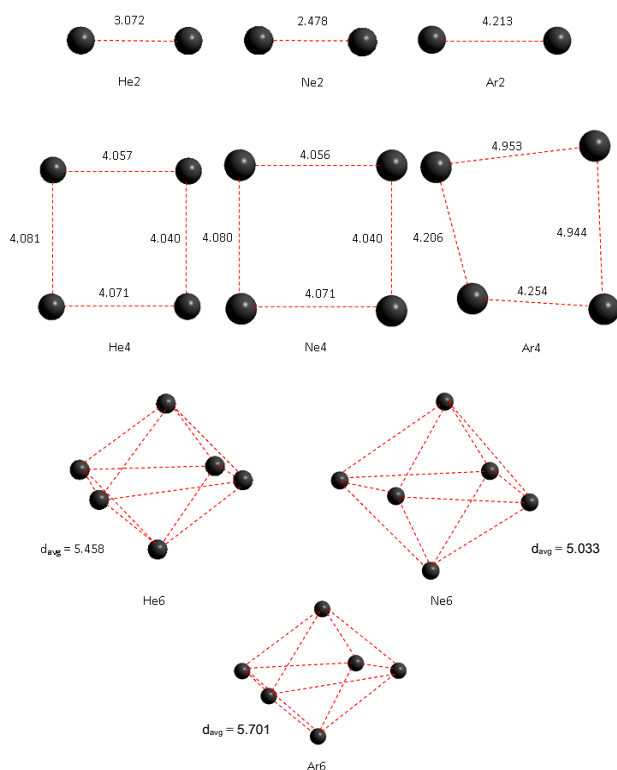


Figure 1. Optimized structure of inert gas clustered system (X_n , $X = \text{He, Ne, Ar}$, $n = 2, 4, 6$).

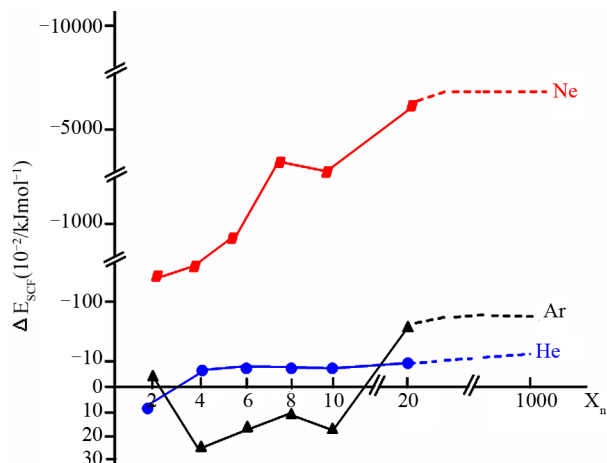


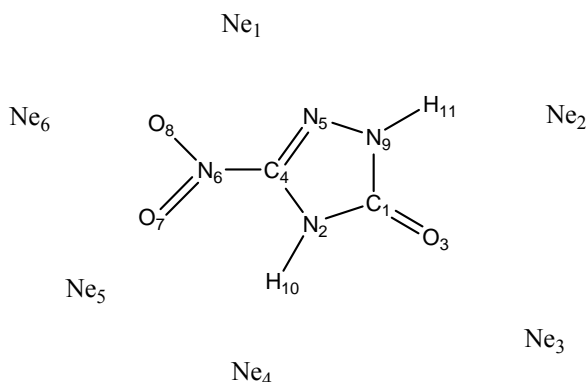
Figure 2. Stabilization on energy of inert gas clustered systems (X_n , $X = \text{He, Ne, Ar}$, $n \geq 2$).

Table 1. Self-consistent field energy of weakly-bound inert gas systems.

Inert gas system	E_{SCF}	ΔE_{SCF}^*	IR frequency [#]
He	-2.9070	0	-
He ₂	-5.8141	0.0735	44.8
He ₄	-11.6282	-0.0053	10.1 - 26.4
He ₆	-17.4423	-0.0079	2.8 - 13.1
He ₈	-23.2564	-0.0184	0.88 - 30.8
He ₁₀	-29.0705	-0.0236	0.81 - 34.2
He ₂₀	-58.1410	-0.0525	0.7 - 19.2
Ne	-128.8944	0	-
Ne ₂	-257.7898	-2.7436	152.2
Ne ₄	-515.5851	-6.1069	8.5 - 26.7
Ne ₆	-773.3768	-9.8089	2.2 - 16.1
Ne ₈	-1031.1721	-45.2899	44.0 - 206.3
Ne ₁₀	-1288.9603	-43.8537	11.1 - 204.3
Ne ₂₀	-2577.9206	-87.8020	1.0 - 208.4
Ar	-527.5171	0	-
Ar ₂	-1055.0343	-0.0105	20.2
Ar ₄	-2110.0685	0.2678	2.2 - 40.0
Ar ₆	-3165.1028	0.0814	1.9 - 21.8
Ar ₈	-4220.1371	0.0289	3.8 - 20.7
Ar ₁₀	-5275.1714	0.1208	1.0 - 24.7
Ar ₂₀	-10550.3431	-0.7509	1.2 - 21.3

* $\Delta E_{\text{SCF}} = [E_{\text{SCF}}(X_n) - nE_{\text{SCF}}(X)] \times 2625.5$, in kJ/mol unit; [#] in cm^{-1} unit

supplementary material). The B3LYP/6-31G (d, p)-calculated molecular thermodynamic energies of all species are presented in **Tables 3-5**. The stabilization effect for all Ne_6 -clustered reactants (with a stabilization energy of around 50 kJ/mol) is more obvious than the corresponding effect in the He_6 -clustered system (**Table 3**).



Scheme 2. Geometry of neon gas clustered-5-nitro-1,2,4-triazol-3-one (NTO_{Ne₆}).

Table 2. Geometrical and vibrational analysis of NTO molecule.

Results* Bond type	Distance	Obs.			Vib. Frequency (Scaled by 0.96)	Obs.		
		a	b	b, c		b(1)	b(2)	d
C ₄ -N ₆	1.442 (-0.35%) [#]	1.443	1.451	1.447	1157	-	1021	1018
C ₁ -N ₂	1.393 (1.09%)	1.380	1.405	1.378	1055 (-2.77%) [#]	1085	1111	1109
C ₁ -N ₉	1.388 (1.54%)	1.374	1.398	1.367	1224 (-2.63%)	1257	1282	1280
N ₉ -N ₅	1.356 (-0.95%)	1.366	1.359	1.369	1375 (2.77%)	1338	1343	1340
C ₄ -N ₂	1.368 (1.41%)	1.356	1.365	1.349	1422 (-2.80%)	1463	1477	1473
C ₄ =N ₅	1.298 (0.62%)	1.299	1.290	1.290	1560	-	-	1541
N ₆ -O ₇	1.224 (0.58%)	1.225	1.214	1.217	1573 (0.64%)	1563	1605	1546
C ₁ =O ₃	1.225 (-0.08%)	1.234	1.203	1.226	1775 (-0.78%)	1789	1716	1712
N ₉ -H ₁₁	1.010	1.009	1.008	0.916	3506 (0.49%)	3489	3200	3198
N ₂ -H ₁₀	1.010	1.009	1.008	0.875	3507	-	-	3242
M. R.E.	0.83%	-	-	-	1.84%	-	-	-

*B3LYP/6-31G (d, p) calculated; [#]Relative error (R.E.), refer to the experimental data in Ref. 34; a:see Ref. 43; b:see Ref. 34, b(1)/Ar matrix and b(2)/thin solid film; c:see Ref. 44; d:see Ref. 33.

3.2. Characteristics of Some Elementary Reactions

The synthesis of NTO from urea was performed in a six-membered rare gas-clustered system (He₆ and Ne₆), the reactions being in the sequence of chlorination, amination, formylation, and nitration, with the adoption of catalysts and corresponding reagents. In addition to the superior stabilization effect that was observed in the neon-clustered system (**Table 3**), comparative analysis of each reaction in which free radical or ionic-type substitution occurred was performed, as discussed below.

Table 3. Self-consistent Field energy of helium and neon clustered reaction systems.

Molecular system	E_{SCF}	Molecular system	E_{SCF}	ΔE_{SCF} *
1Cl ₂ He ₆	-1163.078491	1Cl ₂ + 6He	-1163.077688	-2.1083
2ClradHe ₆	-1163.035446	2Clrad + 6He	-1163.033733	-4.4975
3HClHe ₆	-1163.064750	3HCl + 6He	-1163.063498	-3.2871
3NH ₃ He ₆	-758.835059	3NH ₃ + 6He	-758.833718	-3.5208
4HClHe ₆	-758.84490	4HCl + 6He	-758.843337	-4.1037
5He ₆	-948.635476	5 + 6He	-948.633465	-5.2799
6He ₆	-411.354934	6 + 6He	-411.353427	-3.9566
7He ₆	-948.596018	7 + 6He	-948.594356	-4.3636
8H ₂ OHe ₆	-411.373110	8H ₂ O + 6He	-411.371673	-3.7728
9HNO ₃ He ₆	-615.830430	9HNO ₃ + 6He	-615.828743	-4.4292
9N ₂ O ₃ He ₆	-820.267955	9N ₂ O ₃ + 6He	-820.266964	-2.6019
10H ₂ OHe ₆	-615.866998	10H ₂ O + 6He	-615.865742	-3.2976
10HNO ₃ He ₆	-820.326287	10HNO ₃ +6He	-820.325528	-1.9928
1Cl ₂ Ne ₆	-1919.018086	1Cl ₂ Ne ₆	-1919.001554	-43.4048
2ClradNe ₆	-1918.977538	2Clrad + 6Ne	-1918.957599	-52.3498
3HClNe ₆	-1919.006041	3HCl + 6Ne	-1918.987364	-49.0365
3NH ₃ Ne ₆	-1514.775193	3NH ₃ + 6Ne	-1514.757584	-46.2324
4HClNe ₆	-1514.785991	4HCl + 6Ne	-1514.767203	-49.3279
5Ne ₆	-1704.575934	5 + 6Ne	-1704.557331	-48.8422
6Ne ₆	-1167.297423	6 + 6Ne	-1167.277293	-52.8513
7Ne ₆	-1704.542412	7 + 6Ne	-1704.518222	-63.5108
8H ₂ OHe ₆	-1167.315406	8H ₂ O + 6Ne	-1167.295539	-52.1608
9HNO ₃ Ne ₆	-1371.773810	9HNO ₃ + 6Ne	-1371.752609	-55.6640
9N ₂ O ₃ Ne ₆	-1576.208445	9N ₂ O ₃ + 6Ne	-1576.190830	-46.2482
10H ₂ OHe ₆	-1371.809549	10H ₂ O + 6Ne	-1371.789608	-52.3551
10HNO ₃ Ne ₆	-1576.270748	10HNO ₃ + 6Ne	-1576.249394	-56.0649

* $\Delta E_{SCF} = [E_{SCF}(\text{species} \cdots X_6) - E_{SCF}(\text{species} + 6X)] \times 2625.5$, X = He and Ne, in kJ/mol unit.

3.3. Chlorination of Urea

Chlorine gas was initially cleaved to produce chlorine radicals. Urea was then chlorinated in a neon-clustered and a helium-clustered reaction system, respectively, to prepare N-chlorine urea. The calculation results revealed that a total activation energy of 182.9 kJ/mol was required for chlorine cleavage ($E_{a12radHe6} = 121.5$ kJ/mol) followed by chlorine substitution of an amine hydrogen ($E_{a23HClHe6} = 61.4$ kJ/mol) in the He₆ system, while a total of 173.5 kJ/mol was required for the same reaction to proceed in the Ne₆ system. The energy difference be-

Table 4. Thermodynamic energy of reaction species of NTO synthesis.

Energy* Species	B3LYP/6-31G(d,p)		
	E_{SCF}	H	G
1Cl ₂ He6	-1163.078491	-1162.986885	-1163.093681
2ClradHe6	-1163.035446	-1162.943360	-1163.049030
3HClHe6	-1163.064750	-1162.975878	-1163.078242
3NH ₃ He6	-758.835059	-758.717684	-758.813489
4HClHe6	-758.84490	-758.728555	-758.831724
5He6	-948.635476	-948.478824	-948.587206
6He6	-411.354934	-411.239798	-411.333159
7He6	-948.596018	-948.440155	-948.554078
8H ₂ OHe6	-411.373110	-411.257982	-411.354280
9HNO ₃ He6	-615.830430	-615.710020	-615.818177
9N ₂ O ₃ He6	-820.267955	-820.144442	-820.263175
10H ₂ OHe6	-615.866998	-615.747083	-615.850369
10HNO ₃ He6	-820.326287	-820.201318	-820.317571
1Cl ₂ Ne6	-1919.018086	-1918.925066	-1919.022028
2ClradNe6	-1918.977538	-1918.884995	-1918.976024
3HClNe6	-1919.006041	-1918.916523	-1919.007846
3NH ₃ Ne6	-1514.775193	-1514.656512	-1514.747725
4HClNe6	-1514.785991	-1514.669109	-1514.761627
5Ne6	-1704.575934	-1704.419063	-1704.515776
6Ne6	-1167.297423	-1167.180526	-1167.267036
7Ne6	-1704.542412	-1704.386050	-1704.485649
8H ₂ ONe6	-1167.315406	-1167.199561	-1167.288638
9HNO ₃ Ne6	-1371.773810	-1371.652991	-1371.745242
9N ₂ O ₃ Ne6	-1576.208445	-1576.084565	-1576.188654
10H ₂ OFe6	-1371.809549	-1371.689051	-1371.780684
10HNO ₃ Ne6	-1576.270748	-1576.145535	-1576.243347

* E_{SCF} , H (thermal enthalpy) and G (Gibbs free energy) in au.

Table 5. Thermodynamic energy of reaction species of NTO synthesis (continued).

Energy* Species	B3LYP/6-31G (d, p)		
	E_{SCF}	H	G
1Cl ₂ Ne6FeCl ₃	-4563.256395	-4563.125531	-4563.190213
2ClradNe6FeCl ₃	-4563.235088	-4563.104869	-4563.164119
3HClNe6FeCl ₃	-4563.241093	-4563.112217	-4563.172849
3NH ₃ Ne6FeO	-2853.484392	-2853.333243	-2853.394204
4HClNe6FeO	-2853.481378	-2853.330736	-2853.391812
5Ne6FeO	-3043.210429	-3043.018312	-3043.088748
6Ne6FeO	-2505.932844	-2505.781961	-2505.836291
7Ne6FeO	-3043.263005	-3043.071021	-3043.144449
8H ₂ OFe6FeO	-2505.949772	-2505.797756	-2505.850440
9HNO ₃ Ne6FeO	-2710.512044	-2710.353101	-2710.407649
9N ₂ O ₃ Ne6FeO	-2914.846054	-2914.686007	-2914.737940
10H ₂ OFe6FeO	-2710.498635	-2710.340116	-2710.394519
10HNO ₃ Ne6FeO	-2914.911227	-2914.749782	-2914.801342

* E_{SCF} , H (thermal enthalpy) and G (Gibbs free energy) in au.

tween the above two reaction systems was attributed to the fact that the chlorine radical was separated by 2.284 - 2.435 Å and was distant from the amino H atom by 1.987 - 2.425 Å in the transition complexes (TS_{12radNe6} and TS_{23HClNe6}, **Figure 3**) of the neon-clustered system, while the corresponding distances were shorter in the transition states of the helium-clustered system at 2.544 - 2.648 Å and ~2.436 Å, respectively (TS_{12radHe6} and TS_{23HClHe6}). When a metal chloride catalyst was included in the reaction, a total of 131.8 kJ/mol ($E_{a12radNe6FeCl3} + E_{a23HClNe6FeCl3}$) was required to complete the reaction. Therefore, ferric chloride exhibited a catalytic effect in this chlorination stage (**Figure 3**). Inspection of the molecular geometries of the transition state complexes showed that the two chlorine atoms were separated by only 2.109 Å, and they formed two strong hydrogen bonds (with H-bond distances of 1.843 Å and 1.847 Å) with the amine hydrogen in TS_{12radNe6FeCl3}, stabilizing the molecular system. This suggests that the use of a ferric chloride catalyst is advantageous for optimum progression of the chlorination stage in a neon gas environment.

3.4. Amination of N-Chloro Urea

In the next stage of the reaction, ammonia was used as the amination reagent for the amination of N-chloro urea in helium gas-clustered (3NH₃He6), neon gas-clustered (3NH₃Ne6) and ferrous oxide-catalyzed neon gas-clustered (3NH₃Ne6FeO) systems. The corresponding energy barrier for the introduction of an amino group into the main frame to form semicarbazide hydrochloride was lowest at 135.2 kJ/mol ($E_{a34HClNe6FeO}$) when the reaction proceeded through the FeO catalytic route (3NH₃Ne6FeO → 4HClNe6FeO); hence, ferrous oxide exhibited an obvious catalytic effect for the amination reaction (**Figure 4**). By surveying the molecular structure and atomic charge density, the following observations were made: 1) in 3NH₃Ne6FeO, weak interaction between the Fe and N atoms led to the atomic charge of N being -0.6144, slightly higher than the related charge of -0.6231 in 3NH₃Ne6, which elongated the N-Cl bond by 0.004 Å as compared with the length of 1.739 Å in 3NH₃He6 and 3NH₃Ne6. The more positive N provides a more positive and reactive site for NH₃ to attack. 2) In TS_{34HClNe6FeO}, the electron-withdrawing effect between FeO and the amino H caused N (charge density -0.6086) to favorably combine with NH₂⁻, and a strong bonding interaction will form between the Cl⁻ ion and the ammonia H (Cl⁻···H 1.578 Å); thus, the corresponding interparticulate force stabilized the transition state complex.

3.5. Nitration of 1,2,4-Triazol-3-One

Nitric acid (HNO₃) and dinitrogen pentoxide (N₂O₅)

were used as nitration reagents for the nitration of 1,2,4-triazol-3-one (TO) in non-catalytic rare gas-clustered systems (He_6 or Ne_6) or a catalytic neon gas-clustered system to obtain 5-nitro-1,2,4-triazol-3-one. The reaction using HNO_3 as the reagent and ferrous oxide as the catalyst, which proceeded through electrophilic substitu-

tion via the route $9\text{HNO}_3\text{Ne}_6\text{FeO} \rightarrow 10\text{H}_2\text{O}\text{Ne}_6\text{FeO}$, had an energy barrier of 81.6 kJ/mol ($E_{a910\text{H}_2\text{O}\text{Ne}_6\text{FeO}}$) that had to be overcome: this was lower than the energy barrier in the other reaction systems in which HNO_3 or N_2O_5 was used to nitrate 1,2,4-triazol-3-one in non-catalytic He_6 and non-catalytic Ne_6 environments (Figure 5). By inspect-

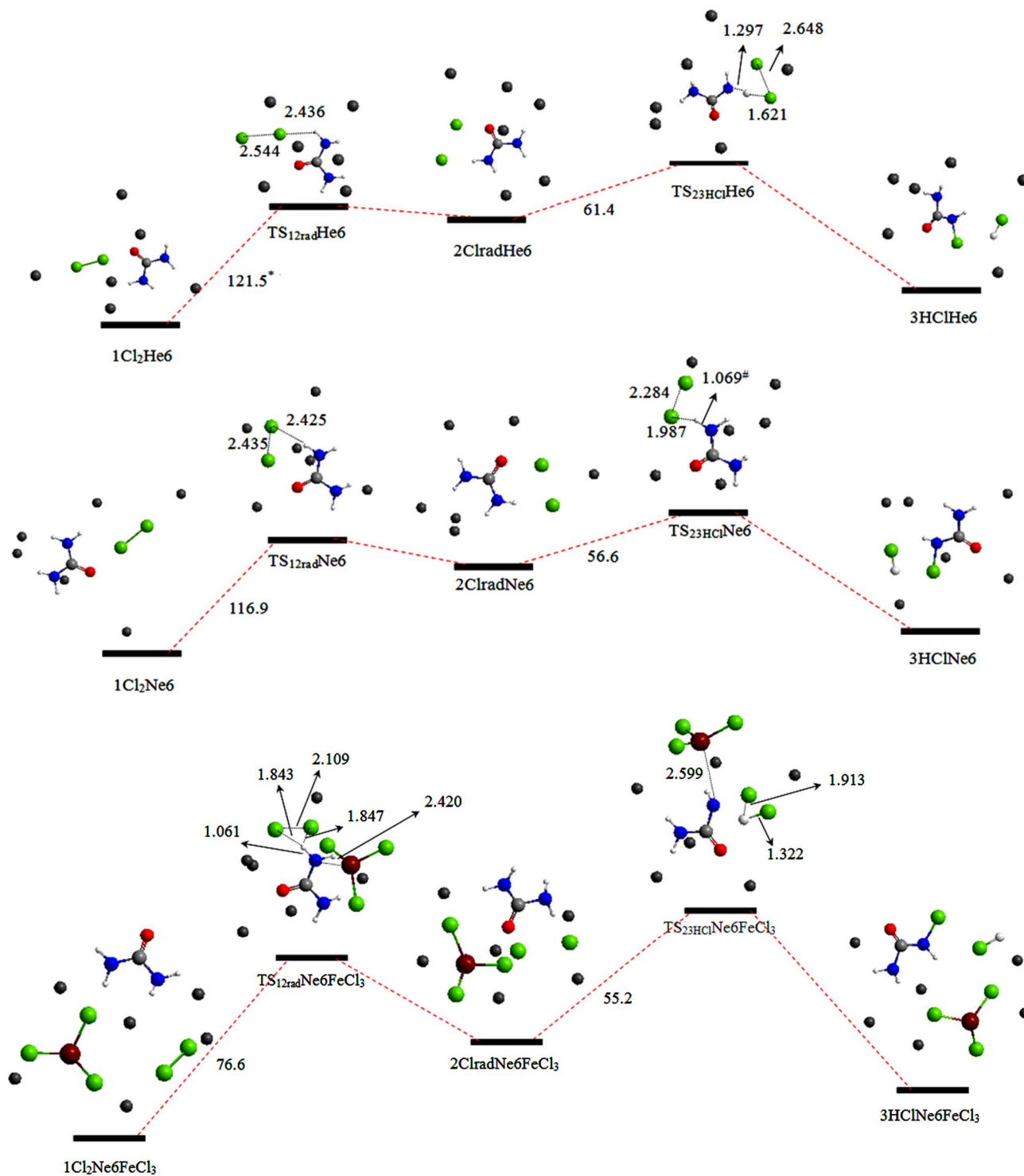


Figure 3. Comparison of chlorination of urea in inert gas clustered system (continued).

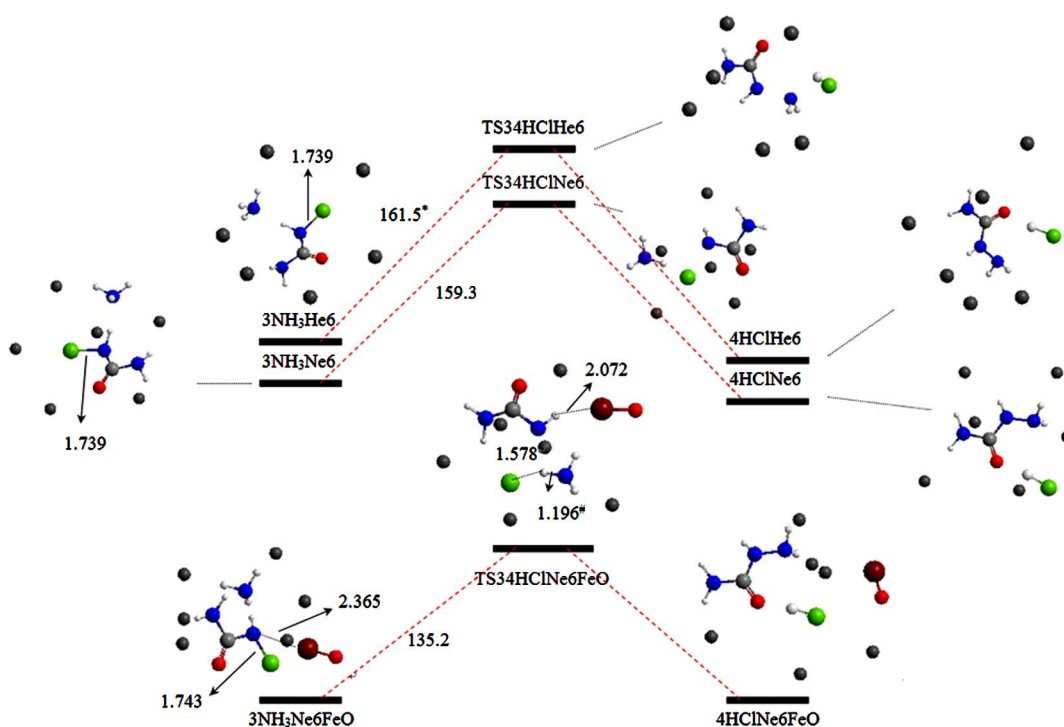


Figure 4. Comparison of amination of N-chloro urea in inert gas clustered system (* activation energy, in kJ/mole; # distance, in Å).

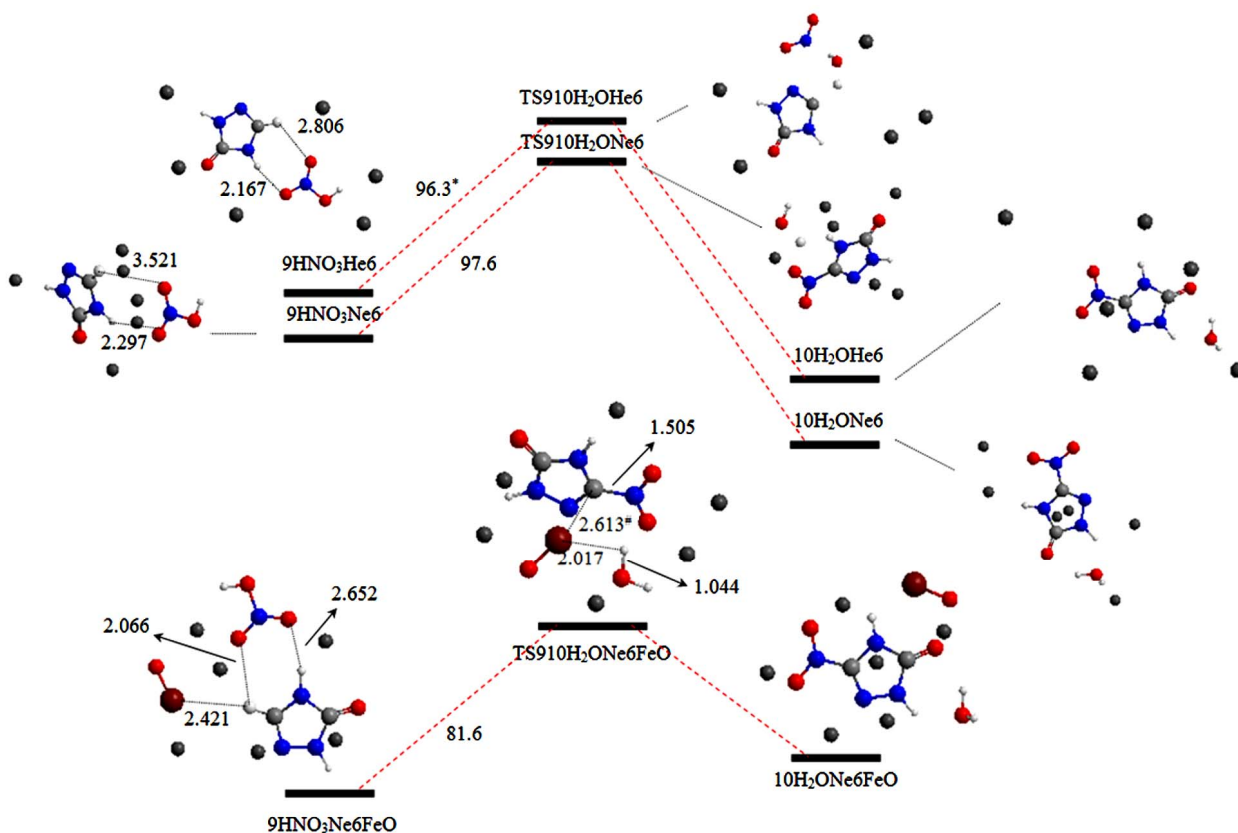


Figure 5. Comparison of amination of N-chloro urea in inert gas clustered system (* activation energy, in kJ/mole; # distance, in Å).

tion of the molecular structure and atomic charge density, the following characteristics were observed: 1) in the reactant system $9\text{HNO}_3\text{Ne}_6\text{FeO}$, the weak interaction between FeO and H (distant by 2.421 Å) resulted in an electron-withdrawing effect of Fe, pulling the H atom away from the 1,2,4-triazol-3-one (TO) mainframe, resulting in the charge density of C (0.2725) being less positive than the related charge density of C in $9\text{HNO}_3\text{He}_6$ and $9\text{HNO}_3\text{Ne}_6$ (0.3001 and 0.354, respectively), thus providing a more reactive site for further NO_2^+ substitution. 2) In $\text{TS}_{910\text{H}_2\text{O}_{\text{ne}6}\text{FeO}}$, the O^- -H anion in HNO_3 directly pulled away an amino H to form H_2O , which then interacted strongly with FeO, and the negatively-charged C atom could then easily combine with the NO_2^+ ion. The whole scheme transition complex scheme indicated that no separate active particles existed, thus resulting in the integrated stability of the intermediate system.

4. Conclusion

Rare gas-clustered systems (X_n , $\text{X} = \text{He, Ne, Ar}$, $n = 2 - 20$) were modeled using a quantum mechanical computation method. Neon-clustered systems were found to result in a greater stabilization energy (ΔE_{SCF}) than the respective helium- or argon-clustered systems owing to the interaction of individual gas atoms. B3LYP/6-31G(d, p)-calculated geometries and vibrational frequencies are close to the experimental values, and therefore this method can be implemented in cases in which experiments are unable to be performed to obtain the related data, especially for precious high-energy-density materials. Another important purpose of this research was the exploration of feasible pathways for the gaseous-phase synthesis of 5-nitro-1,2,4-triazol-3-one (NTO). Indeed, the adoption of theoretical techniques to model molecular reaction systems provides a new method of investigation of the synthesis of specific materials and could offer useful information for reference prior to experiments being performed. The findings revealed the optimum conditions for a series of reactions, and showed for the studied reaction processes that chlorination is feasible in a ferric chloride-catalyzed Ne_6 -clustered system. The results indicated that ferrous oxide is a good catalyst, effectively reducing the energy barrier to promote amination and nitration, and that nitric acid was a suitable nitration reagent. Together, the findings indicated an improved method of NTO synthesis.

5. Supplementary Material

All optimized geometries of reaction species in this work are available.

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