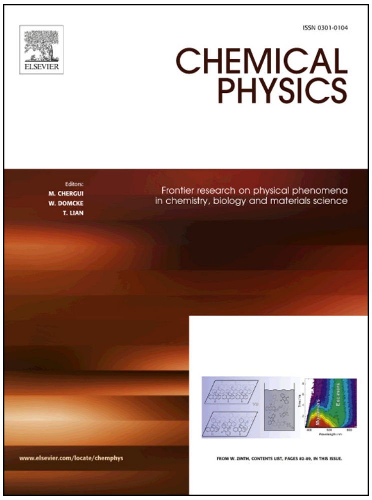

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Exploration for the stabilities of CHN_7 and CN_7^-: A theoretical study on the formation and dissociation mechanisms

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ABSTRACT

CHN_7 and CN_7^- are meta-stable species. In order to study on the relationship between thermodynamic and kinetic stabilities, the potential energy surfaces of CHN_7 and CN_7^- were scanned at the B3LYP/aug-cc-pVDZ level. After the analysis of potential energy surfaces, the optimum pathways were got to conclude the dissociation and formation mechanisms. The dissociation barriers of 5-azido-1*H*-tetrazole and 5-azido-2*H*-tetrazole are about 150 kJ mol^{-1}. They are sufficient to keep the two azidotetrazoles stable. The reaction between cyanogen azide and azide anion cannot produce azidotetrazolate anion, but produce the linear CN_7^- with a lower barrier. The reaction between cyanogen azide and hydrazoic acid preferentially produce 5-azido-1*H*-tetrazole. The decyclization barriers of 1*H*-tetrazolo[1,5-d]tetrazole and tetrazolo[1,5-d]tetrazolate anion are 44.7 and 81.6 kJ mol^{-1}, respectively. The deprotoned anion is more available than the neutral compound. Heptaazacubane and heptaazacubanide anion with cubic geometries are highly unstable.

KEYWORDS

Potential energy surface; reaction mechanism; nitrogen-rich compound; quantum chemistry

1. Introduction

Since the successful synthesis of N_5^+ by Christe *et al.* in 1999 [1], N_8 has been anticipated. Unfortunately, the experimental attempt of reaction between $N_5^+SbF_6$ and CsN_3 was failed, and the theoretical investigation indicated that the electron of *cyclo*-N_5^-, most recently Zhang *et al.* reported the two crystalline states containing it [2, 3], can easily transfer to the V-shaped N_5^+, leading to decomposition [4]. However experimental studies on high nitrogen content species with 56 electrons, *i.e.*, N_7O^+ [5-7], OCN_6 [8-12], CHN_7 [13-21] and CN_7^- [13, 22], achieved some advances.

The experimental effort for formation of N_7O^+, reaction between NF_2O^+ and excess HN_3, was promoted by Christe *et al.*, and the oxygen once was considered at the 4-position [6]. Later, the combinational work, including another experiment of Christe's group and our computation, verified the reaction involved 1-oxo-N_7O^+ instead of 4-oxo-N_7O^+ [7]. Carbonyl diazide with a formula of CN_6O was firstly isolated by Zeng *et al.* [11] The dissociation of carbonyl diazide on the potential energy surface of singlet state is similar as that of 4-oxo-N_7O^+ which has been reported by Zeng *et al.* [23] and us [24], respectively. It involves evolution of dinitrogen on one side and azide group shifting from carbonyl group to nitrogen linked to carbon on the other side, and agrees with the matrix isolation of OCN_4 [25].

5-Azido-1*H*-tetrazole with a formula of CHN_7 can be conveniently synthesized by the reaction between cyanogen bromide and double amount of sodium azide under acidic condition [13, 14]. It can also be formed by using 5-amino-1*H*-tetrazole [15-17], 5-hydrazino-1*H*-tetrazole [18], diaminoguanidinium salt [19] and 4-(1*H*-tetrazol-5-yl)tetraaz-3-ene-2-carboximidamide[20] as starting materials, and the hydrogen atoms are naturally fixed at the 1-position *via* these reactions. According to the crystal structure reported by Stierstorfer *et al.* [14], 5-azido-1*H*-tetrazole crystallizes in a monoclinic unit cell of space group $P2_1$/c. They also found that the total electronic energy of 5-azido-2*H*-tetrazole is lower than that of 5-azido-1*H*-tetrazole by 16.1 kJ mol^{-1} at the MP2/aug-cc-pVDZ level [14]. 5-Azidotetrazolate anion with a formula of CN_7^- can be obtained by adding base to 5-azido-1*H*-tetrazole [22]. Another CHN_7 is the controversial 1*H*-tetrazolo[1,5-d]tetrazole. Taha reported the fused ring compound prepared by 1,5-diaminotetrazole and nitrous acid [21], but it is hard to repeat [26].

These isoelectronic species are marginally stable. It is worthwhile to explore their formation and dissociation pathways. Although the reaction mechanisms of analogue N_7O^+ and CN_6O have been studied sufficiently, there are still some issues on CHN_7 and CN_7^-. Primarily, we need to determine whether or not 1*H*-tetrazolo[1,5-d]tetrazole exists. It is also needed to be illustrated that although 5-azido-2*H*-tetrazole is the dominant isomer thermodynamically, the reaction between cyanogen azide and hydrazoic acid prefers to produce 5-azido-1*H*-tetrazole. More importantly, the previous studies did not