



Reaction mechanisms of 3-amino-4-nitro-furoxan formation by 3-amide-4-nitro-furoxan and sodium hypochlorite in water and benzene solvents

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ABSTRACT

Synthesis of new furoxan-based compounds has been a hot research topic in order to explore the energetic materials with good application prospect. 3-amino-4-nitro-furoxan is a precursor for synthesis of furoxan derivatives because that the amino groups are prone to be substituted by nucleophiles. A theoretical research is conducted for the formation reaction of 3-amino-4-nitro-furoxan by 3-amide-4-nitro-furoxan and sodium hypochlorite in water and benzene solvents using the density functional theory (DFT) and CCSD coupled cluster method to reveal the formation mechanism and explore new synthesis routes. The structures and energies of intermediates and transition states in the possible reaction pathways are given, and the potential energy surfaces of the every reaction channels are mapped. The results indicate that the formation mechanism is mainly through two stages: generation and hydrolysis of isocyanate. Hydrogen bond plays an important role for the hydrolysis process. The formation mechanism is shown to be dependent on the polarity of solvent. The hydroxyl ion (OH^-), originated from the basic properties of sodium hypochlorite solution, is shown to be more likely first attacker than the hypochlorite ion (OCl^-) for the reactant 3-amide-4-nitro-furoxan due to the low active barrier in the polar water solvent. But the OCl^- dominates the reaction in benzene solvent where the isocyanate is formed via the dehydration chlorination by OCl^- and Hofmann rearrangement with the elimination of chloride ion. The isocyanate is then hydrolyzed through addition of a H_2O molecule to the $\text{N}=\text{C}$ double bonds, rotation of the hydroxyl hydrogen, transfer of hydrogen to the N atom in the amide group and the removal of a CO_2 molecule to form the final product. The benzene solvent is more suitable than water solvent for the formation reaction due to the lower active barrier of 46.4 kcal/mol. The reaction is not feasible at room temperature and raising properly temperature of system would be requisite to realize the synthesis reaction.

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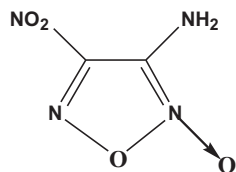
1. Introduction

Furoxan-based energetic materials have attracted considerable interest because of the advantages of high energy density, high standard enthalpy of formation, high nitrogen content, and high level of environmental compatibility [1–3]. They are expected to have potential applications in national defense and national economy [4–6]. Furoxan, a five-membered nitrogen- and oxygen-containing ring with two active oxygen atoms, is an important explosive unit because that the combination of N-oxide and a ‘latent’ nitro-group structure could enhance the detonation performances [5].

At present, synthesis of new furoxan-based compounds has been a hot research topic to explore the energetic materials with good application prospect [7–10]. Single furoxan compounds are precursors for synthesis of various poly-furoxan and macrocycle-furoxan derivatives, which play important roles in the development of furoxan-based energetic materials [11–15]. For the amino or nitro substituted single furoxan derivatives, 3,4-dinitrofuroxan has been synthesized by Godovikova et al. from glyoxime via two steps of nitration and oxidation since 1993 [16,17]. Afterwards, the post-processing method for nitration reaction has been improved by Li et al. [18]. Recently, the formation mechanism of the two-step reaction for the 3,4-dinitrofuroxan has been clarified by our previous work [1]. However, the synthesis and properties of 3-amino-4-nitro-furoxan are fewer reported in experiment and theory. 3-amino-4-nitro-furoxan (Scheme 1) would serve as

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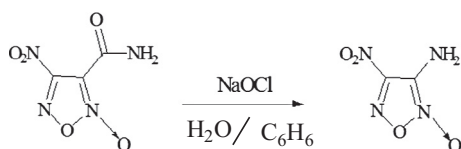
Scheme 1. Molecular structure of 3-amino-4-nitro-furoxan.

an intermediate in the synthesis of other furoxan derivatives because that the amino groups are prone to be substituted by nucleophiles [16,19–21].

In this work, we have carried out density functional theory (DFT) and Coupled Cluster Singles and Doubles (CCSD) method to complete the energetics evaluations of several possible courses for the formation of 3-amino-4-nitro-furoxan leading from 3-amide-4-nitro-furoxan and sodium hypochlorite (NaClO) solution in water and benzene solvents (Scheme 2). Hypochlorous acid (HClO), hypochlorite ion (OCl^-) and hydroxyl ion (OH^-) are considered respectively to be the first attacker for reactant. By mapping the potential energy surfaces (PESs) for the possible pathways, we gain a theoretical understanding of the formation mechanisms and provide the necessary conditions for the experimental synthesis.

2. Computational details

The DFT computations have become an accepted tool for analyzing structure, bonding, reactivity and properties because of its relative cheapness and relative accuracy. The Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP), one of the hybrid functionals, has the advantage of more accurately computing the true total energy due to using both the electronic density and the individual electronic wave functions to compute the total energy. The basis set 6-311++G(d,p) usually leads to satisfactory structures [22]. Therefore, the DFT using the B3LYP functional with 6-311++G(d,p) basis set is chosen to calculate the formation reaction, which have shown that it is successful to predict the properties of energetic materials [23–27]. All geometry optimizations of molecular structures are performed with Gaussian 09 package [28] at the B3LYP/6-311++G(d,p) level. The structural parameters are allowed to be optimized, and no constraints are imposed on molecular structures during the optimization process. All optimized structures are characterized to be the local energy minima on the potential energy surfaces without imaginary frequencies by vibrational analysis. Each transition state has only one imaginary frequency, which has been confirmed by the intrinsic reaction coordinate (IRC) [29,30]. A higher level energy correction, CCSD single-point energy calculation, is performed to get more accurate potential curves [31–33] because it is capable of providing accurate and reliable description of electron correlation for nondegenerate states [34,35]. Besides, the solvent effects of water and benzene are also considered in the self-consistent reaction-field (SCRF) calculations by using the polarizable continuum model (PCM) method [36],



Scheme 2. Reaction courses for calculations. It represents that the formation reaction is analyzed in water and benzene solvent respectively.

which has been proven to be a reliable tool for the description of electrostatic solute-solvent interactions [37,38].

3. Results and discussion

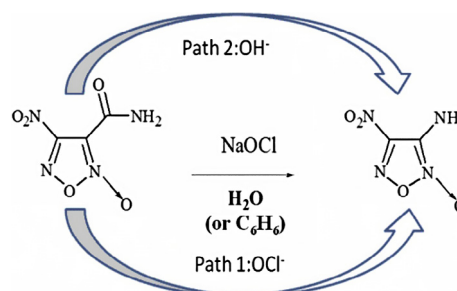
Sodium hypochlorite solution usually exhibits a weak base due to a dynamic balance as shown by the reaction [39,40]:



So the HClO, OCl^- and OH^- may all be involved in the synthesis reaction. A polar water solvent and a non-polar benzene solvent are chosen to explore the effect of solvent polarity on the reaction. The reactant is first considered for halogenation with HClO molecule, but the channel is excluded due to high energy barrier of 86.1 kcal/mol in H_2O solvent and 76.2 kcal/mol in C_6H_6 solvent (see Fig. S1 in Supporting Information). So the formation reaction is considered as the following two possible routes: one is started by OCl^- (path 1) and the other is started by OH^- (path 2) as shown in Scheme 3.

3.1. Reaction mechanisms in water solvent

The free energy profiles for the formation of 3-amino-4-nitro-furoxan, leading from 3-amide-4-nitro-furoxan reacted by OCl^- in water solvent, are shown in Figs. 1 and 2. The optimized geometries of reactants, intermediates, transition states, and products in the process are presented together. The calculated free energy and relative free energy for all species involved in the reaction pathway at the CCSD/6-311++G(d,p)//B3LYP/6-311++G(d,p) levels are shown in Table 1. The IRC paths of the transition states involved in the reaction are given as well in Supporting Information (Fig. S2) to ensure the accuracy of transition states. The pathway begins with the chlorination reaction of the 3-amide-4-nitro-furoxan via the transition state 1 (TS1), where the chlorine atom in OCl^- attacks on the acylamino nitrogen atom, while hydrogen atom on acylamino group transfers to the oxygen atom in OCl^- to form a hydroxyl ion, with an intermediate 1 (IM1). This process is exothermic by 0.62 kcal/mol with a high barrier height of 59.1 kcal/mol. Following the chlorination reaction, the next step is the Hofmann rearrangement of IM1, with the removal of a hydrogen chloride (HCl) to form an important intermediate isocyanate (IM2). The barrier height for this rearrangement process (TS2) is predicted to be 62.4 kcal/mol and exothermic by 15.2 kcal/mol. The formation of isocyanates via Hofmann rearrangement has been recognized in the previous reports [41,42]. The isocyanate occurs then hydrolysis via TS3, where one of the nitrogen carbon double bonds ($\text{N}=\text{C}$) is opened so that the hydroxyl and the hydrogen in a H_2O molecule are added respectively to the carbon atom and the nitrogen atom in the $\text{N}=\text{C}=\text{O}$ group, leading to the formation of the IM3. The bond lengths related to the reaction in the TS3 have been given in configuration, which are consistent with the previous



Scheme 3. Proposed possible routes on the formation of 3-amino-4-nitro-furoxan from 3-amide-4-nitro-furoxan via two initial attackers OCl^- and OH^- .

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