Commun. Comput. Chem. Vol.**2**, No.**2**, pp.54-60
doi: 10.4208/cicc.2014.v2.n2.2 June 2014

COMMUNICATION

Theoretical Study of the Nitration Mechanism of Furoxan by Dinitrogen Pentoxide

Junxia Ding[1*] , Weipeng Lai[2] and Xiaofang Chen[1]

[1]*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China, P. R. 116023*

[2]*Computer-Aided Energetic Materials Design Group, Xi'an Modern Chemistry Research Institute, 168 Zhangba Road, Xi'an,710065, P. R. China*

Received 20 May 2014; Accepted (in revised version) 13 June 2014

Abstract: The high accurate theoretic method is performed to investigate the nitration mechanism of furoxan by dinitrogen pentoxide. We demonstrate that the nitronium ion is the active species in furoxan nitration. The nitration process including two main steps: the two hydrogen atoms on carbon are replaced by nitronium ion respectively. The energy barrier of the second nitration step is higher than the first one. Each nitration step is characterized by the nitronium ion attacking and the proton elimination step. For the first nitration step the proton elimination process has a higher energy barrier than the nitronium ion attacking step, but for the second nitration step the result is just the reverse.

AMS subject classifications: 92Exx

Key words: Nitration Mechanism, Furoxan, Dinitrogen Pentoxide

Furoxan(1,2,5-oxadiazole-2-oxides) is a five-membered nitrogen oxygen heterocycles with coordination of an oxygen atom**.** The high nitrogen contents and the potential nitro group make the furoxan derivatives to be the outstanding energetic materials. Over the last decade, the synthesis of furoxan derivatives has attracted considerable interest due to their potential applications in pharmacolog [1], argochemistry [2] and high energy density materials involving explosives [3]. The 3,4-dinitrofuroxan compound is one of the most important derivatives for functional furoxan derivatives. As shown in **Figure 1**, the two added nitro

* Corresponding author. *E-mail address*: jxding@dicp.ac.cn (J.-X. Ding)

groups reduce the component of hydrogen atom and provide better oxygen balance, so the explosion pressure can be increased. More important, the nitro group in 3- and 4- position is known to be prone to be replaced by nucleophile [4-8], so it can be the excellent intermediate to synthesis other furoxan derivatives. So far, the experimental synthesis for 3,4-dinitrofuroxan is rare [9-11].

Nitration reaction is one of the most common types in organic chemistry. It is of interest because of its own characteristics as an electrophilic substitution. Investigations of the nitration have been chiefly concerned with the reaction mechanisms. Nitration can be effected under a wide variety of conditions. The characteristics and kinetics exhibited by the reactions depend on the reagents that used. Dinitrogen pentoxide (N_2O_5) was the common clean nitrating agent which has been widely used in nitration reaction. Thus, dinitrogen pentoxideis was choose as the nitrating agent in the current paper. The aim of this paper is to study the nitration mechanism of furoxan with dinitrogen pentoxide to produce 3,4-dinitrofuroxan by employing theoretical calculation method. The B3LYP method (Becke's three parameter nonlocal exchange functional [12–14] with the nonlocal correlation functionalof Lee, Yang, and Parr [15])has been proved suitable to study the furoxan and its substituted derivatives[16]. So the B3LYP method with 6-311G(d,p) basis set was employed to study the reaction mechanism of furoxan with dinitrogen pentoxide. In order to get more accurate potential curves, CCSD method was performed in the single point calculation as well [17-19]. Besides, the solvent effect was also considered in the SCRF calculations by using the PCM method [20], water was choose as the solvent. The Gaussian 09 program was employed for all of the computations [21].

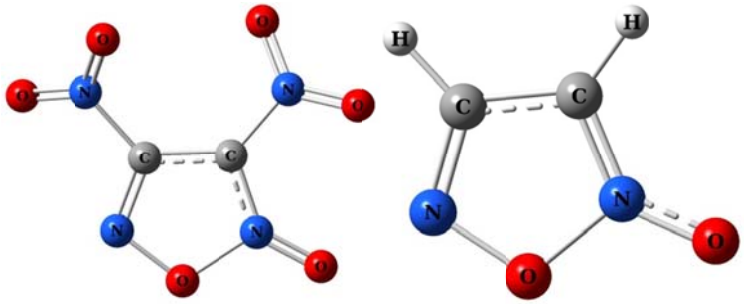

Figure 1: The stable structure of the furoxan and 3,4-dinitrofuroxan

Normally, solid dinitrogen pentoxide exists as (NO_2^+)(NO_3^-). Solutions of dinitrogen pentoxide in water show some ionization to nitrate and nitronium ion. Euler and other workers have been suggested that the nitronium ion was the active species in nitration reaction [22]. Thus, we first consider the reaction of nitronimu ion with furoxan. As we known, the nitration reaction is typical electrophilic substitution reaction. In order to confirm the accurate reaction sites, the natural charge for furoxan molecule and NO_2^+ was