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Theoretical Study of the Nitration Mechanism of Furoxan by Dinitrogen Pentoxide

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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

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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].

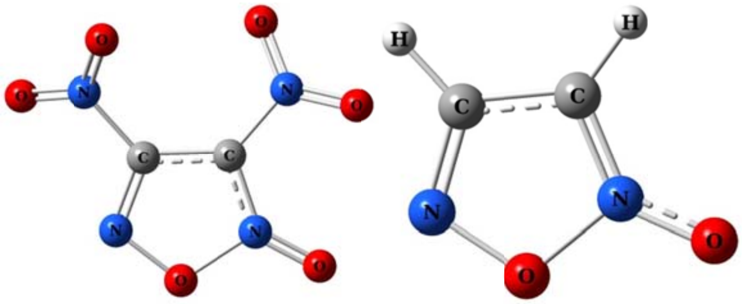


Figure 1: The stable structure of the furoxan and 3,4-dinitrofuroxan

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 investigated by NBO analysis, the result was shown in **Figure 2**. It is clear that 1C atom presents negative charge comparing with 2C atom, and 7N atom shows positive charge comparing with 6N atom. Consequently, electrophilic reaction will prefer to take place first on 1C atom rather than 2C atom.

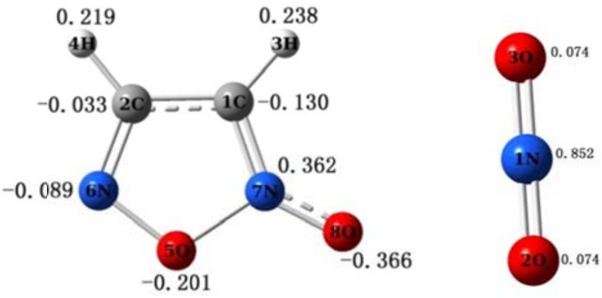
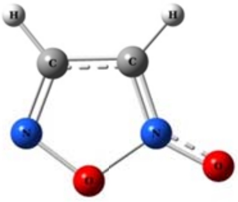
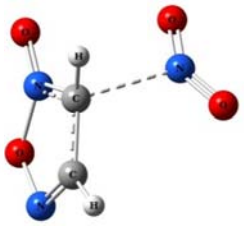


Figure 1: The natural charge for furoxan and nitronium ion molecule

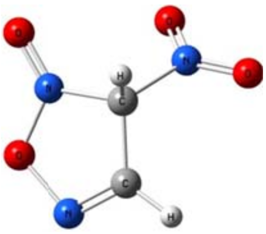
The optimized geometries of the reactants, intermediates, transition states and product were shown in **Figure 2**. Vibrational frequencies of all species were calculated at the B3LYP/6-311G(d,p) level. All the stationary point were identified for local minima (number of imaginary frequencies =0) and transition state (with one imaginary frequencies =1).The calculated electronic energy and relative energy for all species involved in the nitration of furoxan at the B3LYP/6-311G(d,p)//CCSD/6-311++G(d,p) level were shown in **Table 1** as well.



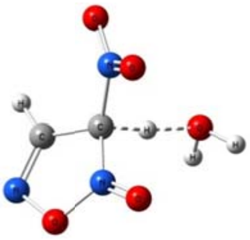
Furoxan



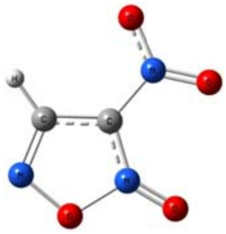
TS1



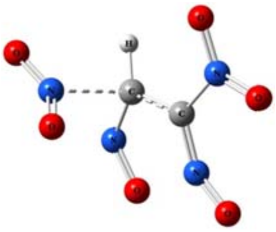
IM1



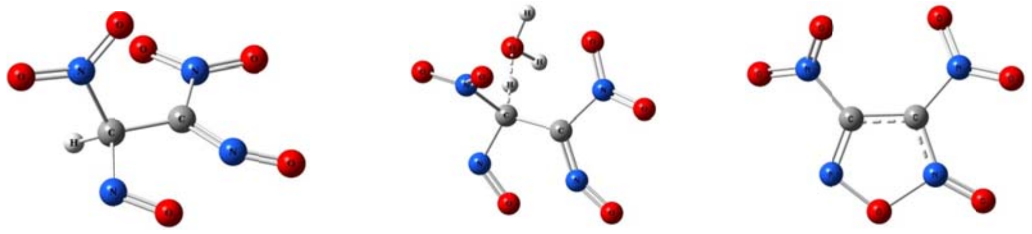
TS2



IM2



TS3



IM3 TS4 3,4-dinitrofuroxan

Figure 3: All the optimized geometries of the stable point (reactant, transition states, intermediates and product) involved in the nitration of furoxan at the B3LYP/6-311G(d,p). The dash line represented the vibrational vector of the imaginary vibrational frequency.

The energy profile for the nitration of furoxan to form the 3-4-dinitrofuroxan was shown in **Figure 4**. As can be seen from **Figure 4**, two main steps are involved in the nitration of furoxan: the hydrogen on the 1C and 2C atom is replaced by nitronimu ion respectively. Each nitration step passed through two-step transition states. At the initial step, the 1C atom of fuxozan is attacked by the N atom of nitronimu ion, leading to the intermediate of IM1. This step via a transition state of TS1, which has a barrier height of 21.54 kcal/mol in water solvent. Then, under the help of water molecule, via the second transition state of TS2, the proto is removed from the carbon atom forming the stable IM2. TS2 has a barrier height of 26.21 kcal/mol, which is little higher than the TS1. From **Figure 3** we could find that, as the N atom of nitronimu ion moving toward furoxan, the hydrogen atom on the 1C offset the plane of furoxan molecule gradually, forming a dihedral angle of 58^{o} in IM1. Moreover, the bond length of 1C-7N is 1.378 Å and 1.495 for TS1 and IM1, which is lengthened by 0.05Å and 0.175 Å respectively when compared with that of stable fuxozan. At the same time, the 1C-2C bond and 1C-3H bond are also lengthened at TS1 and IM1. This illustrated the interaction between 1C and 7N or 2C decreased while the interaction between 1C and 1N strengthened gradually. In addition, when nitronimu ion attacked the 1C atom, the angle ONO of nitronimu ion is changed from 180^{o} to 144^{o} in TS1 and 129^{o} in IM1. This shown the nitronimu ion became to nitrate ion. The IM2 is an arenium ion, which in a subsequent step undergoes proton elimination process to form the stable nitro group. This step needs the necessary base, which might be proton acceptor. Here we used the water as the proton acceptor and forming the hydronium ion. This step should overcome an energy barrier of 26.21 kcal/mol which is little higher than the former nitronimu ion attacking step. The second nitration substitution step is the same to the first step, passing through two transition states: TS3 and TS4. However, these two transition state has much higher energy barrier than the first nitration step. The TS3 and TS4 have the energy barrier height of 44 kcal/mol and 33kcal/mol respectively. This might be duo to the steric-hinerance effect.

Beyond that, the energy barrier of the proton elimination step is higher than the nitronimu ion attacking step, this is much different from the first nitration step as well, The final product is the 3,4-dinitrofuroxan, with the energy of 5.66 kcal/mol lower than the reactant.

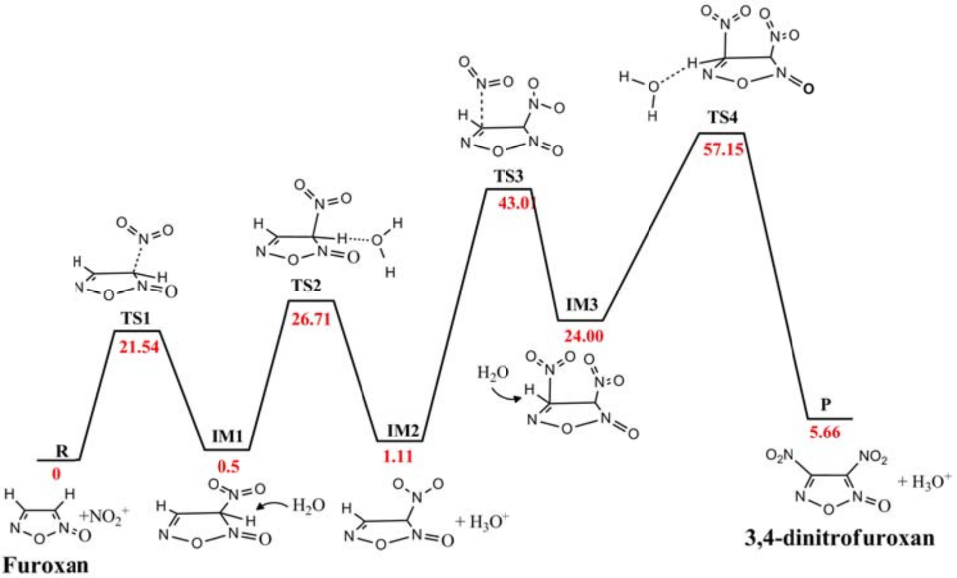


Figure4 : Energy profile for the nitration of furoxan with dinitrogen pentoxide at B3LYP/6-311G(d,p)//CCSD/6-311++G(d,p) level

Table 1 Calculated electronic energy (E_0) and ZPE(zero point energy) for all species involved in the nitration of furoxan at the B3LYP/6-311G(d,p)//CCSD/6-311++G(d,p) level. The ZPE corrected energy ΔE and the imaginary frequency is presented as well.

	E_0(au)	ZPE(au)	CCSD(au)	CCSD+ZPE (au)	ΔE(Kcal /mol)	Imaginary Frequency
NO_2^+	-204.9180405	0.01045	-204.453001	-204.4425489	0	
H_3O	-76.8761499	0.03527	-76.6835438	-76.6482788	0	
Furoxan	-337.3110828	0.0494	-336.464496	-336.4150976	0	
TS1	-542.2157868	0.0613	-540.884615	-540.8233136	21.54	249.1
IM1	-542.2248038	0.06319	-540.920043	-540.8568533	0.5	
TS2	-618.6958776	0.08445	-617.172746	-617.088294	26.71	390.11
IM2	-541.8522188	0.05173	-540.532536	-540.4808056	1.11	
TS3	-746.7344049	0.06214	-744.918723	-744.85658	43.01	266.63
IM3	-746.7401682	0.06331	-744.950193	-744.8868832	24.00	
TS4	-823.2086394	0.08467	-821.191929	-821.1072624	57.15	430.96
3,4-dinitrofuroxan	-746.3833315	0.05357	-744.594609	-744.5410353	5.66	

In conclusion, we use the theoretical method to study the nitration mechanism of furoxan by dinitrogen pentoxide. The nitronium ion is the active species in furoxan nitration. The nitration process including the two hydrogen atoms are replaced by nitronium ion respectively. Each step is characterized by the nitronium ion attacking and proto elimination step which via two transition states respectively. As for the first nitration step the proton elimination process need overcome a higher energy barrier than the nitronium ion attacking step. While for the second nitration step the energy barrier for the nitronium ion attacking step is higher than the proton elimination step.

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