Computational Study of Photooxidation of 1,1-dimethylhydrazine by nitromethane

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Abstract

We have proposed a mechanism of photooxidation of 1,1-dimethylhydrazine with nitromethane in the triplet state. The point of interest in this reaction is reactivity of nitromethane, which is different in different excited states. We determined some energetic properties using MCSCF and DFT methods with 6-311G(d) basis set for all atoms. The interaction between nitromethane and 1,1-dimethylhydrazine in the triplet state proceeds very quickly (the activation energy is 3.5 kcal·mol^{-1}). Products of this reaction are N-metylmethaneimine, molecular hydrogen, and molecular nitrogen, and dimethylamine.

Keywords: nitromethane; 1,1-dimethylhydrazine; photooxidation; triplet; CASSCF, AIM theory

Introduction

A molecule of nitromethane has some probability to transfer to the excited state, S_1. After intersection crossing into the triplet state (T_1) the molecule earns an ability to initiate radical reactions. So, in the triplet state nitromethane interacts with 1,1-dimethylhydrazine abstracting the H-atom. To detail the nitromethane reactivity in the triplet state we have performed some calculations in the frame of Bader AIM theory [1, 4].

The mechanism of this reaction could help us to understand the features of the same reactions with nitro group, such as elimination and polymerization.

The oxidation can proceeds using catalysts and high temperature or high pressure [2]. But the main products are molecular nitrogen and CO_2.

Computational details

The geometries and physical properties were studied by ab initio methods using Gaussian03 [3]. Initial calculations were performed by CASSCF(6,6)/6-311G(d) and by uB3LYP/6-311G(d) for radical reactions. Visualization was produced using Avogadro program. Bader's theory of Atoms in Molecules calculations were performed by Multiwfn-3.3.7 [5].

Results

The nitromethane molecule is shown on Fig. 1. Interatomic distances and bond angles of nitromethane are summarized in Table 1.

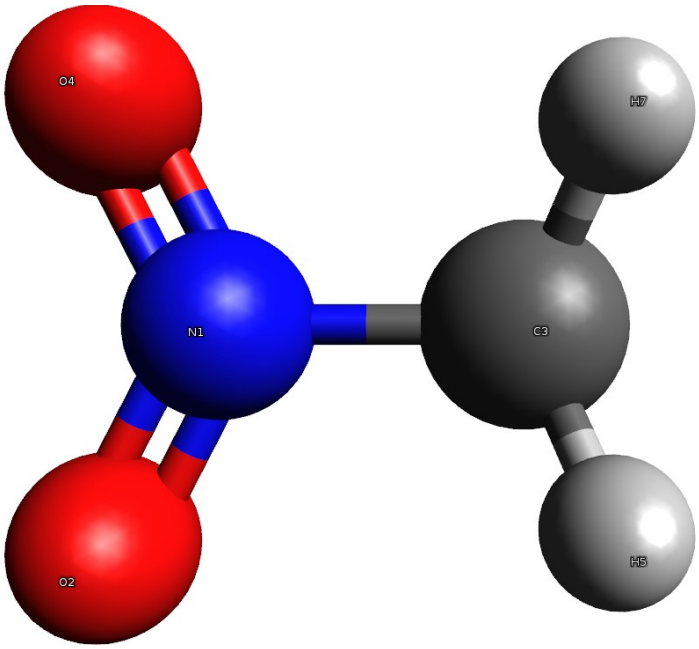


Fig. 1: nitromethane

Table 1: Experimental and calculated bond lenghts and angles of nitromethane

Structural parameter	Experimental value [6]	CASSCF(6,6)/6-311G(d)	UB3LYP/6-311G(d)	UHF/6-311G(d)
r(C-N) *)	1.489	1.475	1.503	1.482
r(N-O) *)	1.224	1.218	1.220	1.185
r(C-H) *)	1.088	1.077	1.090	1.076
a(HCH) **)	107.2	112.0	110.5	112.9
a(ONO) **)	125.3	125.2	126.0	125.9

*) – interatomic distances, in Å ; **) – valence angles, in deg

We conclude that the accuracy of CASSCF method is fairly well. There was no experimental data on the triplet state nitromethane geometry, and we believe that our CASSCF calculations give true results in the triplet state, too. In the triplet state the geometry varies as shown on Fig. 2.

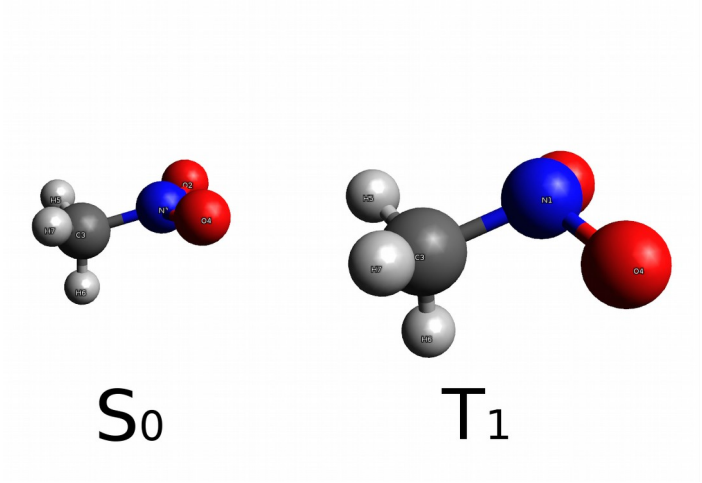


Fig. 2: singlet-triplet geometry modification

Atomic charges were calculated by the Voronoi deformation density (VDD) population analysis are given in Table 2.

Table 2: VDD charges of the nitromethane molecule

Atom	Electronic state	
	Singlet	Triplet
N	0.373	0.047
O	-0.295	-0.101
O	-0.295	-0.101
H	0.070	0.050
H	0.060	0.040
H	0.060	0.050
C	0.016	0.032

It looks like a dissipation of atomic charges, so the molecule earns the great oxidative ability. To test this conclusion we have calculated the contour maps of $\nabla^2\rho$ shown on Fig. 3 and 4.

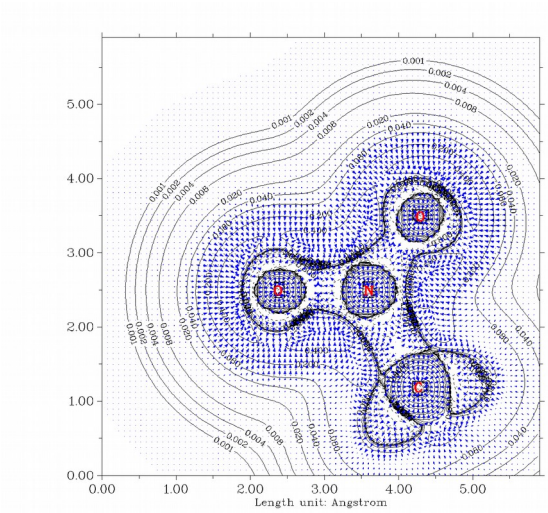


Fig. 3: Contour map of Laplacian of electron density of the nitromethane in the singlet state

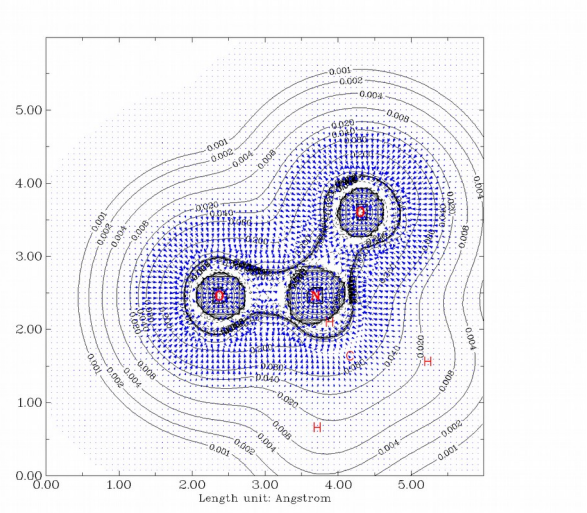


Fig. 4: Contour map of Laplacian of electron density of the nitromethane in the triplet state

Blue arrows mean gradient of electron density functions, black ones denote isolines of $\nabla^2\rho$ — Laplacians of electron density. It can be seen that the concentration of electron density near the oxygen atom basins in the singlet state denotes pure reactivity. In the triplet state the electron density is spread near the oxygen atom basins denoting unpaired electrons existence. There are another relieves of the electron density near attractors (oxygen atoms) shown on Fig. 5 and 6.

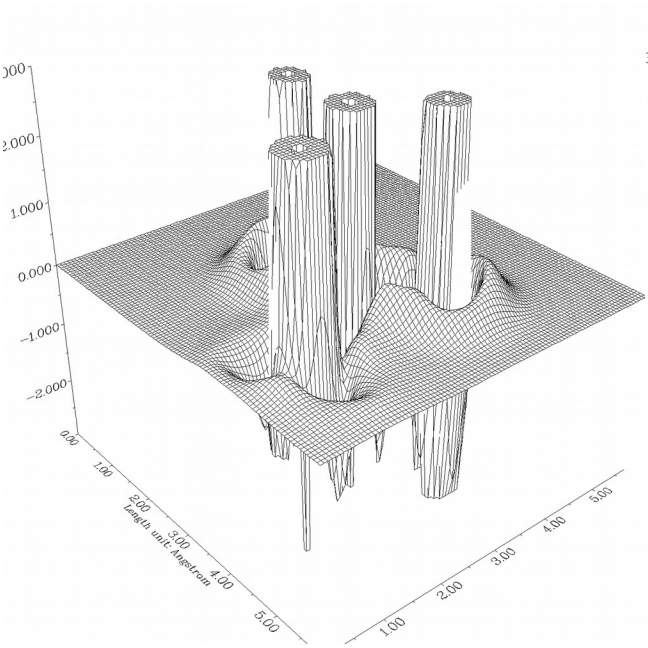


Fig. 5: Relief map of Laplacian of ED of nitromethane molecule in the singlet state

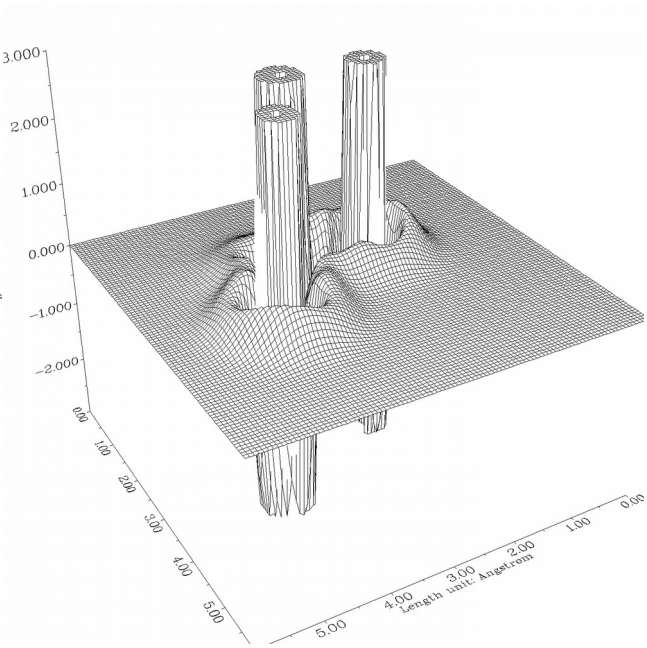
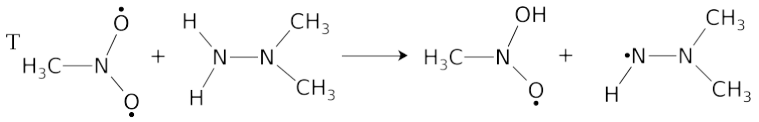


Fig. 6: Relief map of Laplacian of ED of nitromethane molecule in the triplet state

The rods are the atom attractors and it's $\nabla^2\rho \rightarrow \infty$, the peaks near atoms mean the electron density dissipation.

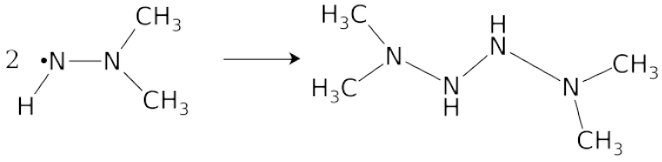
We proposed a mechanism of the reaction that is represented by the reaction scheme 1-4.

At the first stage there has place an abstraction of a hydrogen atom by the triplet state nitrocompound molecule.

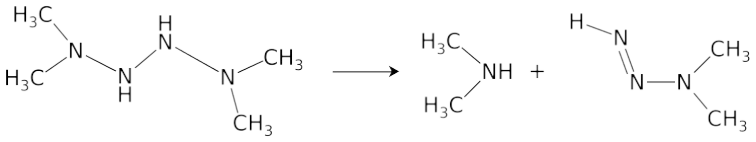


(1)

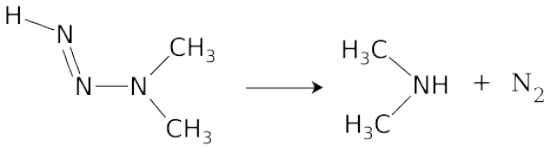
The enthalpy of reaction **1** is -26.5 kcal·mol^{-1}, but the enthalpy of the same reaction in the case of the singlet nitromethane is +7.7 kcal·mol^{-1}. The activation energies are 3.5 kcal·mol^{-1} in triplet state and 30.9 kcal·mol^{-1} in singlet state.



(2)

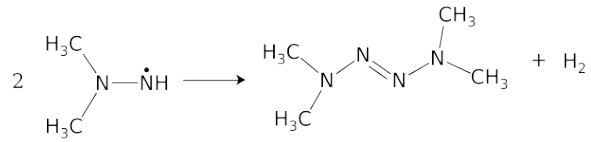


(3)



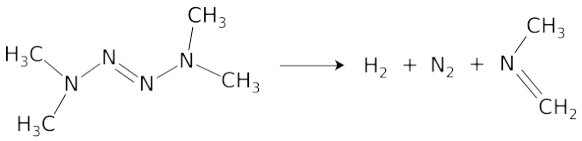
(4)

The activation energy of reaction **3** is 36.9 kcal·mol^{-1} and of reaction **4** is 28.5 kcal·mol^{-1}. This is the preferred reaction path, but as we can see in the case of reaction **5** the dimethylhydrazine radicals can produce 1,1,4,4-tetramethyltetrazene and molecular hydrogen.



(5)

After that the molecule of 1,1,4,4-tetramethyltetrazene produces molecular nitrogen and hydrogen and the N-methylmethaneimine as shown in reaction **6**.



(6)

The activation energy of this reaction is very high *ca*. 66.6 kcal·mol^{-1}.

Conclusions

We have presented some details of the mechanism of photooxidation of 1,1-dimethylhydrazine with nitromethane in the triplet state. Using AIM theory we revealed reactivity of the nitromethane molecule in the triplet state. After excitation, near atom attractors form the peaks of $\nabla^2\rho$. So, the oxygen atoms are centers of the radical attack.

Our suggestion is presented by scheme 1-6 with nitromethane as an oxidation agent. So, this reaction is an example of a low temperature oxidation.

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