Theoretical study of photooxidation of ammonia by nitromethane

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Abstract

Nitrocompound in the excited states reacts as a strong electron acceptor. We have examined its behaviour in reaction with a strong electron donor such as ammonia using CASSCF(6,6)/6-311G* and uB3LYP/6-311G* methods. The mechanism of this reaction consists of hydrogen atom transfer from NH_3 to nitrocompound. In the triplet state the enthalpy of the reaction is of -21.2 $kJ\cdot mol^{-1}$ which is quite low. As a result, there are two radicals being able to interact with other molecules in the system. One possible reaction pathway is NH_2 radicals recombination resulted in hydrazine formation. The second reaction is the nitrocompound abstraction of hydrogen atom from ammonia. The product of this reaction will be nitrosomethane. This reaction was investigated by the Bader theory. It shows an opportunity of interaction and electron density localization via the reaction between nitrocompound and amine.

Keywords: photochemistry nitrocompound ammonia calculations bader photooxidation casscf nitromethane

Introduction

Some quantum chemistry calculations revealed the existance of a triplet state near the excited singlet state for aliphatic nitrocompounds [1]. As a reference organic nitrocompound we took the nitromethane. On the UV/VIS [2] spectrum for gas-phase nitromethane it is a peak near 267nm with logarithm epsilon is 1.2. It corresponds to the $S_1(n,\pi^*)$ state. At CASSCF(8,7)/6-311G* vertical excitation energies are close to the experimential results: 331nm or 3.75eV. The TD-DFT/6-311G* calculation predicts the excitation energy 3.48eV or 356nm.

Computational details

The geometries and physical properties were studied by NWChem-6.6 [3] program using CASSCF(10,10) and CASSCF(6,6) methods with 6-311G* basis sets. Visualization was produced by Avogadro 1.2.0 [4], [5] program. All Bader theory calculations and visualizations were produced using Multiwfn-3.3.7 [6] (Linux edition) program. The plots was provided by Gnuplot program [7]

Discussion

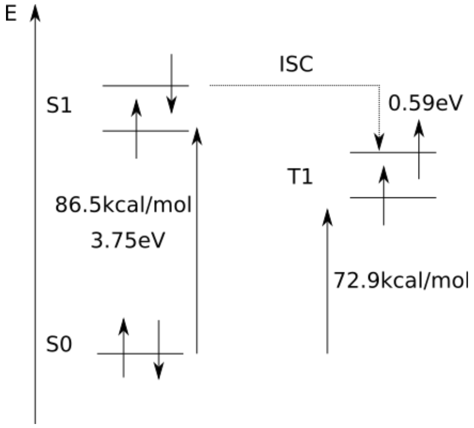

Figure 1: The energy diagram of the nitromethane molecule

As mentioned before the nitromethane molecule has S_1 state near the T_1 state. In the Figure 1 we can see the electron levels for nitromethane molecule. Due to the small energy gap between the singlet and triplet excited states the intersystem crossing (ISC) will proceed fast and effectively. As we have explained previously [8], the nitromethane has a different geometry in the triplet and singlet state.

In the triplet state the nitrocompound represents a radical. On both oxygen atoms the electrons are localized. Consequently the nitromethane molecule can react as a strong electron acceptor. Now we would like to take a look at the reaction between nitromethane and ammonia.

In ammonia it is a very strong N-H bond: the dissociation energy is 435 kJ·mol^{-1} [9]. We can expect the same activation energy for reaction with nitrocompound. The reaction pathway in the triplet state is present in the Figure 2. The reaction path was restored by Nudged Elastic Band method. As we can see, the activation energy is extremely high. The value is 370.8 kJ/mol. This may occurs due to the high N-H bonding. We take a look at the electron density (ED) during the reaction. The Localized Orbital Locator (LOL) would be a representive for this interactions.

On the Figure 3a the LOL function has a very high value between nitrogen and hydrogen atoms of the ammonia. Comparing with the Figure 3a on the 3d the LOL function between oxygen an hydrogen atoms of the nitrocompound is less. During the reaction the bonding of the hydrogen with nitrogen atom is greater than with oxygen atom. On the Figure 3b and 3c there are transfer geometries involved in the investigated reaction. Obviously, the reaction proceeds without a charge transfer.

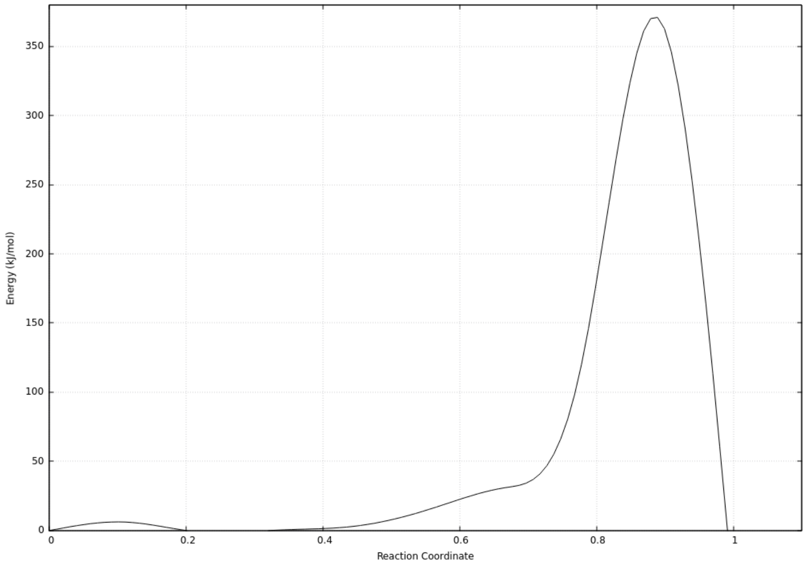

Figure 2: The reaction pathway between ammonia and nitromethane in the triplet state

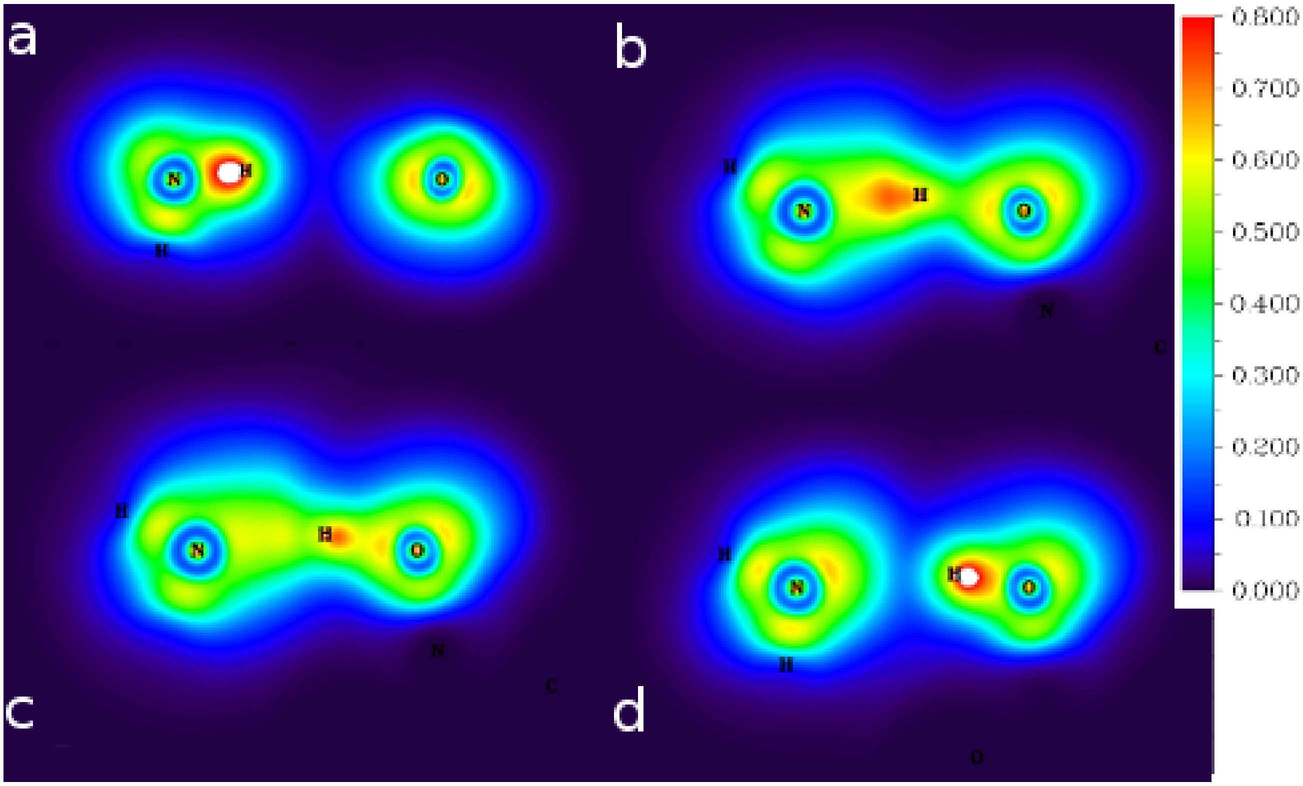

Figure 3: The Localized Orbital Locator function during the reaction between nitromethane and ammonia in the triplet state

The question about active space of the compound is quite difficult. In the Table 1 the occupancies of the orbitals in the active space are presented. In the first column there are the occupancies for the (10,10) active space and in the second column – for the (6,6) active space. The selection of the active space is provided by the rule [10]: 0.02 ≤ “occ’’ ≤ 1.98; “occ’’ is the occupancy number. For the nitromethane reaction with ammonia the selection of the active space with 6 electrons on the 6 orbitals must be right.

CASSCF	(6,6)	(10,10)
E, Hartree	-299.926372	-299.974444
17MO		1.981
18MO		1.980
19MO	1.980	1.978
20MO	1.968	1.967
21MO	1.000	1.009
22MO	0.999	1.001
23MO	0.031	0.003
24MO	0.019	0.002
25MO		0.001
26MO		0.001

Table 1: Calculated occupancies of the molecular orbitals (MO) of the ammonia-nitromethane compound with different active spaces

The reaction preceded by the ammonia inversion. It may be the negative factor for the reaction with nitromethane.

Conclusion

The reaction between nitromethane and ammonia in the triplet state were examined. It proceeds with extremely high activation energy of 370.8 kJ·mol^{-1} and a quite low enthalpy of the reaction -21.2 kJ·mol^{-1}. As we described in our previous publication [8] the reaction between nitrocompound and 1,1-dimethylhydrazine proceeds with a very low activation energy. The difference in activation energies may be explained in terms of Bader theory. On the N-H bond in the ammonia the electron density concentration is high consequently the hydrogen abstraction is difficult. During the reaction in the transition state we can see the strong bonding of the hydrogen atom with nitrogen atom of the ammonia.

Nitrocompound in the triplet state is not able to react with the ammonia molecule in the standard state.

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