Modeling the photoreduction of amines by the triplet nitromethane

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Abstract: Photoreduction of ammonia, methylamine and phenylamine by the triplet nitromethane has been investigated. Using uB3LYP/6-311g* method the geometry of the transition states, pre- and post-complexes was established. The mechanism of photoreduction is quite simple: it is the hydrogen atom abstraction. The N-H-bond of amine breaks and H-atom passes to the nitrocompound. This reaction yields two radicals. Calculated activation energy of the reaction between nitromethane and ammonia is of 3.17 kcal·mol^{-1}. This one is much lower comparing to the reported earlier by us. The EOM-CCSD/cc-pVDZ method predicts activation energy of 2.57 kcal·mol^{-1}. The next examined reaction is the reaction between the triplet nitromethane and methylamine. The mechanism is the same. Calculated activation energy is of 1.17 kcal·mol^{-1}. Due to the methyl group presence it is the energy drop relatively to the first reaction. Some pictures of the electron density are included in the article. Comparing the radicals the phenylamine with nitromethane has been implemented. Calculated activation energy is of 1.51 kcal·mol^{-1}. Hence phenyl group enhances the activation threshold of the proton abstraction. The reaction mechanism is the same hydrogen atom abstraction.

Keywords: photoreduction, amines, nitrocompound, excited state, hydrogen abstraction

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Introduction

Photochemical hydrogen abstraction is one of the most interesting processes in photochemistry. It could be observed with the ketone-like structures having C = O or N = O fragments. One of the most important condition is a small singlet-triplet gap. The excitation must be proceeded *via* a (n,π*)-transition more than *via* a (π,π*)-transition. The corresponding structures are, e.g., ketones, quinones and nitrocompounds. Present work takes into account excited nitrocompounds reacting with some of the amines. Amines could be a donor of the hydrogen atom.

Computational details

All DFT calculations were performed by NWChem [1] program. uB3LYP/6-311g* method was used. The Coupled Cluster [2] calculation were performed by PSI4 [3] program. Visualization of the molecules provided by Avogadro [4], [5] program using OpenBabel [6] code. Topology and electron density descriptors were calculated and visualized by Multiwfn [7] program. Graphs are builded by gnuplot program [8].

Results and discussion

The first reaction researched is hydrogen atom abstraction from monomethylamine by triplet nitromethane. This mechanism is important for many photochemical reactions [9], [10]. It was reported

previously [11] that activation energy for this reaction has extremely high value of 370.8 kJ·mol^{-1}. The reaction pathway represents abnormally plain profile of Potential Energy Surface (PES) with three minima's. But recalculated reaction pathway on the uB3LYP/6-311G* level of theory shows contradictory form. As we can see on fig. 1, new reaction pathway is a classical profile of PES with two minima's of pre- and postreaction complexes and shape of the Transition State (TS) peak. The activation energy is of 24.5 kJ·mol^{-1} (5.9 kcal·mol^{-1}). The peak position on the fig. 1 looks like that activation energy should be above 25 kJ·mol^{-1}, but the graph was smoothed by gnuplot program; barrier calculated by NEB method is of 24.5 kJ·mol^{-1}. Using frequencies task, the Zero-Point Energy-corrected (ZPE) value calculated as 13.3 kJ·mol^{-1} (3.2 kcal·mol^{-1}).

The EOM-CCSD/cc-pVDZ calculations on the geometries obtained by DFT method were performed using PSI4 program . Due to some technical problems, we are not able to obtain ZPE-corrected energies. Calculated activation barrier is of 10.7 kJ·mol^{-1} (2.3 kcal·mol^{-1}).
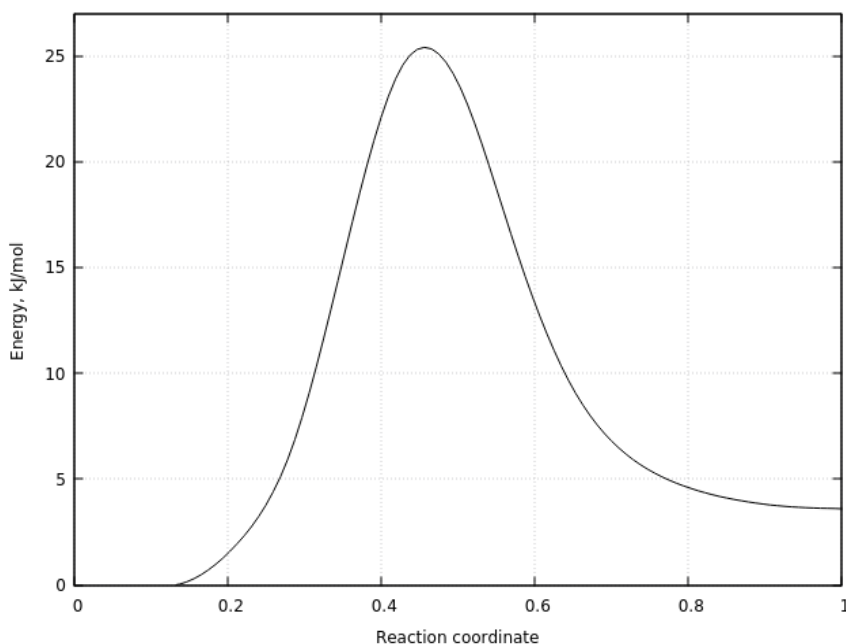

Figure 1: The reaction pathway between ammonia and nitromethane in the triplet state calculated using uB3LYP/6-311G* method

The mechanism of the reaction is the photochemical hydrogen abstraction by the triplet nitromethane. On the fig. 2 we can see the transition state of the corresponding reaction. The enhanced N-H bond length of 1.25 Å of the ammonia corresponds to the reaction pathway. Let us note the geometry of the nitromethane. The NO_2-group plane lays outside of the C-N-O plane. In the singlet state two planes C-N-O^1 and C-N-O^2 are coplanar. It raises the effect discussed below.
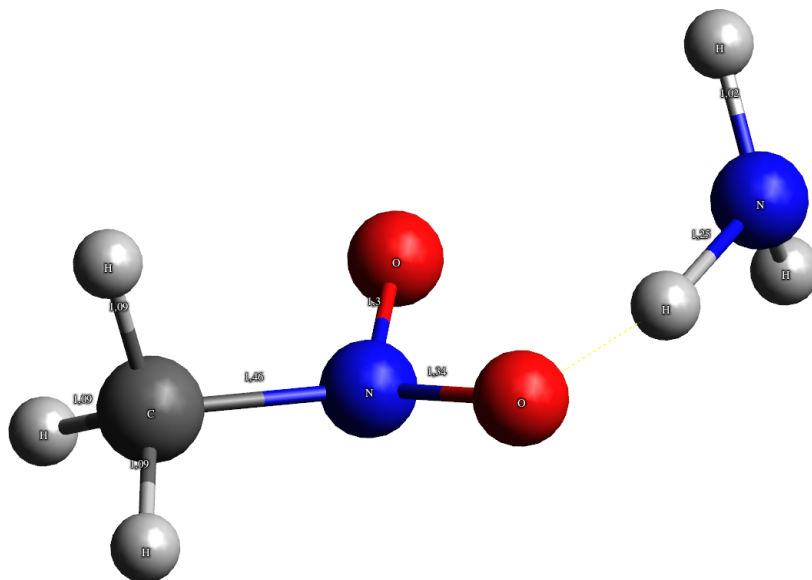
Figure 2: Transition state geometry of the reaction between ammonia and nitromethane

The TS of the reaction between ammonia and nitromethane using the AIM theory was examined. On the fig. 3 we can observe some critical points of the (3,-1)-type. The critical point number 21 is obviously for the TS, but the point number 20 is not. As you can see, this point connects the O2 and N5 atoms. The length of this bond is 2.35 Å. It can be considered as it is the hydrogen bond. Hence rupture of the bonds connecting the post-complex demands more energy than hydrogen abstraction. The point number 19 (type (3,+1)) spawns to satisfy the Poincare-Hopf rule [12]:

atom poins - bond points + ring points - cage points = 1

11 − 11 + 1 − 0 = 1

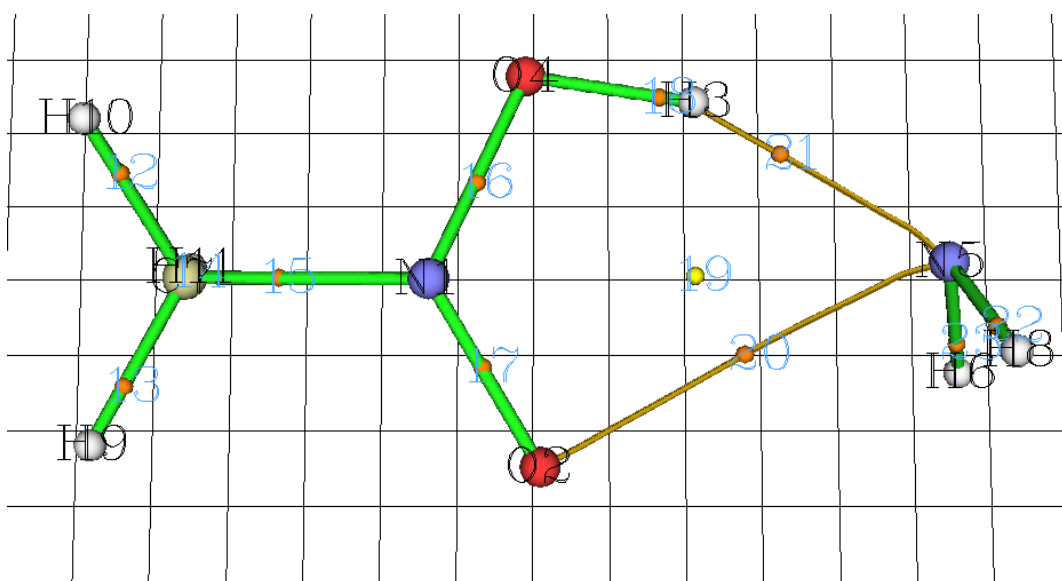*Figure 3: Topology of the TS between ammonia and triplet nitromethane. Orange balls are the (3,-1) critical poins, yellow ball is the (3,+1)-type point*

The second reaction is the methylamine and triplet nitromethane interaction. The mechanism is the same as. Due to the presence of methyl group contrary to the ammonia molecule, we can expect drop of the activation energy. So the ZPE-corrected activation barrier is of 4.9 kJ·mol^{-1} (1.2 kcal·mol^{-1}). The difference between this energy and an activation energy of the previous reaction is 8.4 kJ·mol^{-1}.

On the fig. 4 you can see the Localized Orbital Locator (LOL) spread for the TS between monomethylamine and nitromethane. Violet color means no LOL on the current point and white color means that LOL value is greater than 0.8. Blue contour line denotes Van-der-Waals radius of the system. N label on the top of the picture is nitrogen atom of monomethylamine. Consequently, N label below denotes nitrogen atom of the NO_2 group. Between left oxygen atom and upper nitrogen atom you can see the hydrogen atom proceeding to the nitrocompound from the NH_2 group. Now take a look at the right-side oxygen atom. Slightly decreased LOL areas near the atom denotes electron pairs, are seen on the nitrogen and two pairs on the oxygen. One of the electron pairs on the right oxygen interacts with the nitrogen atom of the methylamine. The nature of that bonding we can guess as donor-acceptor.

The reaction between phenylamine (aniline) and triplet nitromethane was investigated. The mechanism of this process is the same as hydrogen abstraction by nitromethane. The expected plain geometry of the aniline molecule is not present; NH_2 group lays in the other plane than benzene ring.

The activation energy of the reaction is of 6.3 kJ·mol^{-1} (1,51 kcal·mol^{-1}). As expected, this value is less than energy of the reaction with ammonia, but greater than with the monomethylamine.
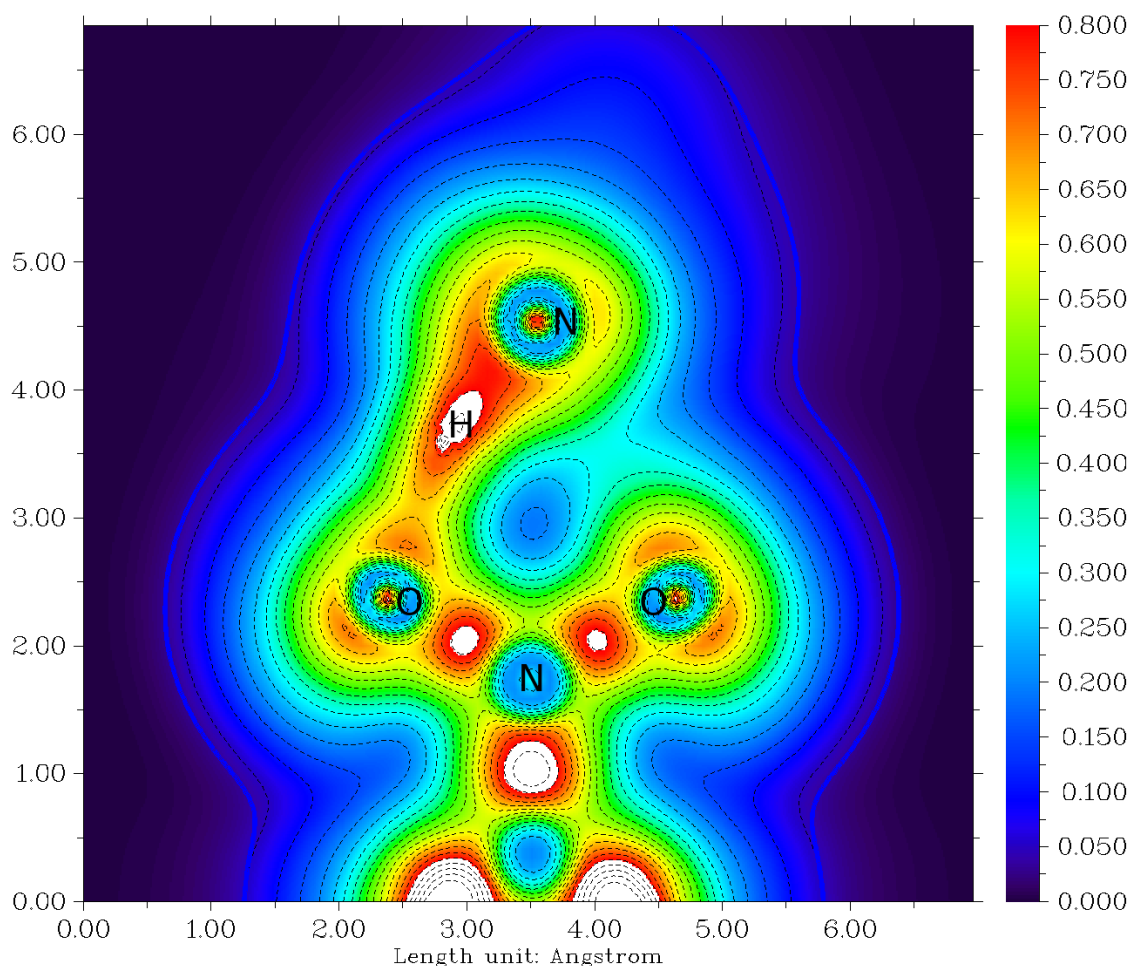
Figure 4: Localized Orbital Locator of the TS between monomethylamine and triplet nitromethane

Conclusions

Some reactions between excited nitromethane and amines were investigated using DFT method calculations. The predicted values for the activation energies are extremely low. But the strong coupling between nitrogen and oxygen atoms was found. It would be the more strong barrier for the next step of the reaction. The resulting reactions are

$CH_3NO_2 + NH_3 \rightarrow CH_3NO_2H\cdot + \cdot NH_2$	$E_a = 13.3$ kJ·mol^{-1}
$CH_3NO_2 + NH_2CH_3 \rightarrow CH_3NO_2H\cdot + \cdot NHCH_3$	$E_a = 4.9$ kJ·mol^{-1}
$CH_3NO_2 + NH_2Ph \rightarrow CH_3NO_2H\cdot + \cdot NHPh$	$E_a = 6.3$ kJ·mol^{-1}

Acknowledgments

Abbreviations

PES   Potential Energy Surface

EOM-CCSD   Equation Of Motion Coupled Clusters Singles and Doubles

DFT   Density Functional Theory

TS   Transition State

ZPE   Zero Point Energy

NEB   Nudged Elastic Band

AIM   Atoms In Molecules

LOL   Localized Orbital Locator

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