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Photoreduction Mechanism of Nitromethane in the Presence of Dimethylamine: A Quantum Chemical Study †

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Abstract

A mechanism of photoreduction of an aliphatic nitro compound—nitromethane—in the presence of a hydrogen donor, dimethylamine, was proposed. Quantum chemical calculations (using the ωB97X-D3/def2-TZVPP method in ORCA) were performed to determine the thermodynamic parameters of the proposed reaction steps. Changes in enthalpy and Gibbs free energy were computed for 12 possible elementary steps, with three key reactions selected for further analysis. Transition states for these key steps were located and reaction energy profiles constructed. The lowest activation energy (6.5 kcal/mol) was found for the hydrogen atom transfer from the methyl group of dimethylamine, while some other stages proceeded without an activation barrier. It was shown that the OH group does not detach directly from the nitrogen atom but through a cascade of rearrangements, including hydroxyl migration. The reaction occurs only for aliphatic nitro compounds due to the presence of an α-hydrogen, which is absent in aromatic analogs. The final mechanism consists of 5 consecutive steps and supports the hypothesis about the specific role of the triplet state of nitromethane in reductive photochemical processes. The study highlights the significance of intramolecular rearrangements in lowering activation barriers. These findings may serve as a basis for further design of light-induced reduction pathways for nitro-containing compounds.

Keywords: nitro compounds; photoreduction; triplet state; dimethylamine; quantum chemical calculations; activation energy; aliphatic compounds; radical particles; reaction mechanism; hydrogen transfer

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1. Introduction

The chemistry of nitro compounds has received significant attention in both practical and theoretical aspects. Nitromethane is one of the simplest representatives of this class of compounds. Photochemical reduction of such substances in the presence of molecules is particularly important.containing amino groups. Special attention is paid to the resulting particles have nitrogen-nitrogen bonds. This reaction may be important for the synthesis of such structures.

Nitroalkanes are colorless liquids with boiling points high for their molecular weights: nitromethane boils at 101.2 °C. Both oxygen atoms in the nitro group are located at an equal distance from the nitrogen atom (0.122 nm), and the angles C—N—O are 120°. This is evidenced by the data of the electron diffraction method and X-ray diffraction analysis. At the same time, it should be borne in mind that the standard length of the N—O simple bond is 0.136 nm, and the N=O double bond is 0.115 nm. The lifetime of nitro compounds (NC) in excited singlet states is close to 10–12 s. During this time, the excited NC molecule either passes into the triplet state due to intersystem crossing (ISC), or isomerizes to organic nitrite. This rearrangement can be carried out both photochemically and thermally. Recent studies have shown that although the activation energies of the forward and reverse reactions are close, the transition from one to the other is difficult, since its activation energy is 167.4–209.2 kJ/mol, and therefore the reaction is easier to carry out photochemically [1–3]

Reactions involving aliphatic NC have been studied much less than with aromatic ones. This is due to the low quantum yields of molecules in the triplet state. The quantum yield of photodegradation of nitromethane (NM) in the C–N bond reaches 0.29. The EPR method confirmed the presence of NO_2 particles during photolysis of NM. The decomposition reaction of aliphatic NC on the C–N bond under the action of light is considered to be the main one. For example, for NM, it occurs at a wavelength of 193 nm and has been studied in sufficient detail in a number of experimental and theoretical papers. In the literature, this reaction is associated with the (σ,σ^*) transition. In the NM –amine system, the C–N bond can be broken with a sufficiently high activation energy when the amine is oriented to the methyl group and without the action of light. Calculations performed by the MP4 method predict the activation energy value of 50.0 kcal · mol^{-1}. NM is also capable of forming hydrogen bonds in solutions, for example, with primary alcohols: ethanol, propanol-1, butanol-1. Similarly, aliphatic NC forms bonds with acids and ions.

Another possible reaction is of interest, the photo–reduction of NC to an amine. In this case, the nitro group will behave like a nucleophile and attach a hydrogen atom from various molecules. To do this, NC undergoes an (n,π^*) transition, as a result of which the lone pair of electrons of the nitrogen atom is distributed over the nitro group. Thus, the reactivity of NC increases. In the works of scientists from different countries, it was reported that a similar reaction occurs in the presence of amines much faster than in the presence of other compounds: alcohols, thiols, etc. Previously, work was carried out to study the possibility of transferring a hydrogen atom from an amine to NC in a triplet electronic state. An interesting fact has been established: the transfer of a hydrogen atom from a methyl group is less preferable than the transfer from an amino group. This is explained by the formation of an additional bond between the NC oxygen atom and the amine nitrogen atom. In this case, the activation energy of the hydrogen atom transfer is significantly reduced. A similar behavior was found in phosphorus compounds. Representatives of groups 4 and 6 of the Periodic Table do not exhibit similar properties.

Despite the large number of works related to such reactions, it is impossible to find a common reaction mechanism in the literature. Usually, the authors of the papers propose various catalysts or photocatalysts, but there is no consensus on the reaction scheme. This work is devoted to the study of the mechanism of interaction of triplet nitromethane with dimethylamine as the simplest representatives of their classes of compounds. It is known that in such systems, the reaction can proceed under the influence of UV light without adding a catalyst.

The history of the study of the reduction of nitro compounds dates back to the work of N.N. Zinin, who in 1842 for the first time carried out the reduction of nitrobenzene to aniline using ammonium sulfide. This discovery marked the beginning of the development of the aniline paint industry.

In modern chemistry, special attention is paid to photochemical processes involving nitro compounds. It has been established that the primary act is the excitation of a molecule, after which the process can proceed in several directions.

The photodissociation of nitro compounds is characterized by the breaking of the C-N bond with an activation energy of about 57 kcal/mol. For aliphatic compounds, this process is predominant [2].

Photo-reduction of nitro compounds occurs through a triplet state. The quantum yield of triplet formation is 0.6–0.8, regardless of the type of triplet state. In the triplet state, the nitro group acquires the properties of a biradical, which significantly increases its reactivity.

1. Studies have shown that the nature of the reaction depends on the type of nitro compound
2. Aromatic compounds are characterized by the formation of azo- and azoxy compounds
3. Aliphatic compounds are predominantly exposed to the breaking of the C-N bond

The environment plays an important role in the photo-restoration process. The presence of amines significantly accelerates the reaction compared to alcohols and thiols. In an alkaline environment, the yield of reduction products increases due to lower oxidative potentials of alcoholic anions [4–7].

Modern research confirms the involvement of the triplet state in the mechanism of photo-healing. This is confirmed by the following facts:

1. Sensitizers naphthalene and benzophenone accelerate the reaction
2. Triplet extinguishers, such as perfluoroaphthalene, suppress the process
3. Molecules in the (n,π*)-triplet state are most easily restored [8–11]

Despite a significant amount of research, the mechanism of photo-reduction of aliphatic nitro compounds remains poorly understood. Most of the works are devoted to aromatic systems, while the behavior of aliphatic compounds requires further study.

Of particular relevance is the study of the effect of the structure of the nitro compound on the reduction mechanism, the search for effective catalysts and the development of process control methods [9–17].

2. The Experimental Part

- Research methodology

All quantum chemical calculations were performed using the ωB97X-D3/def2-TZVPP method in the ORCA software version 5.0.3. The revPBE method based on def2-SVP was used to search for transition states.

- The main hypothesis

It is assumed that the photo-reduction of triplet nitromethane in the presence of dimethylamine proceeds through a series of successive stages with the formation of intermediate radical particles.

- Features of the reaction mechanism

The study showed that the process includes the following stages:

1. The first stage is the formation of radical particles (activation energy 6.5 kcal/mol): $^{3}CH_3NO_2 + HN(CH_3)_2 \rightarrow CH_3NO_2H\cdot + HNCH_2CH_2\cdot$
2. The second stage is the transfer of a hydrogen atom (activation energy 22.9 kcal/mol): $^{3}CH_3NO_2 + CH_3NO_2H\cdot \rightarrow CH_3NO_2H_2 + \cdot CH_2NO_2$
3. The third stage is the separation of hydrogen from the methyl group: $CH_3NO_2H_2 + {}^{3}CH_3NO_2 \rightarrow \cdot CH_2NO_2H_2 + CH_3NO_2H$ (activation energy 11.94 kcal/mol)
4. The fourth stage is the regrouping with migration of the online group: $\cdot CH_2NO_2H_2 \rightarrow OHCH_2NOH$ (it flows without an energy barrier)
5. The fifth stage is the final break in communication: $OHCH_2NOH \rightarrow CH_3NO + \cdot OH$ (it flows without an energy barrier)

The thermodynamic characteristics of the studied reactions are shown in Table 1.

Table 1. Energy parameters of key reactions.

Reaction	**ΔrH°, kJ·mol^{-1}**	**ΔrG°, kJ·mol^{-1}**
Radical formation (1)	−56.32	−59.03
Hydrogen transfer (2)	+92.31	+91.28
Hydrogen separation from the methyl group (3)	−119.90	−116.10

- An important observation

The reaction is possible only for aliphatic nitro compounds due to the presence of alpha-hydrogen. Initially, it was assumed that the separation of the OH group occurs directly from the nitrogen atom, but studies have shown that the process proceeds through the intermediate formation of a hydroxyl group in the methyl group.

- Visualization of the reaction mechanism

The reaction mechanism is clearly shown in Figures 2–5, which demonstrate the transition states and energy profiles of the key stages.

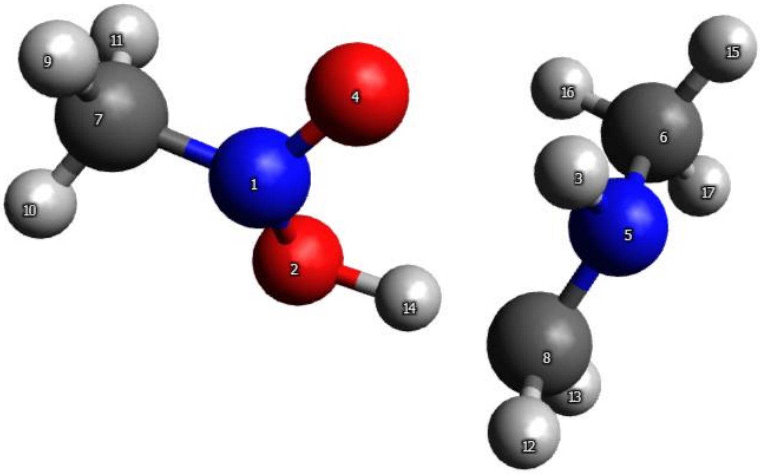

Figure 1. The transition state for the first reaction.

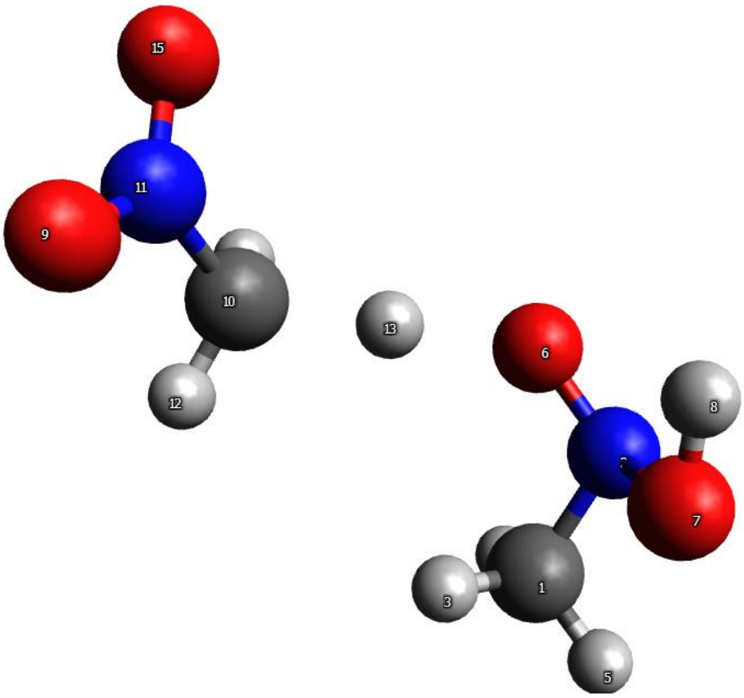

Figure 2. The transition state of the second reaction.

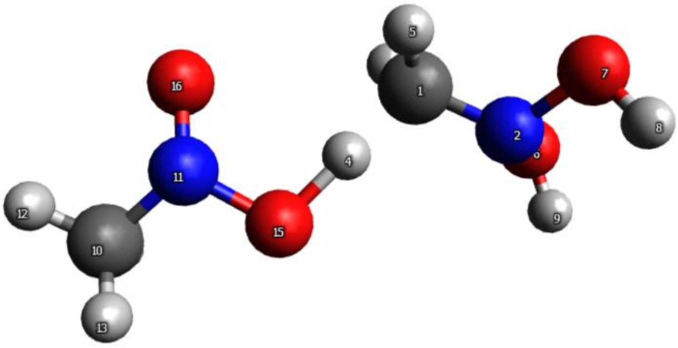

Figure 3. The transition state for the third reaction.

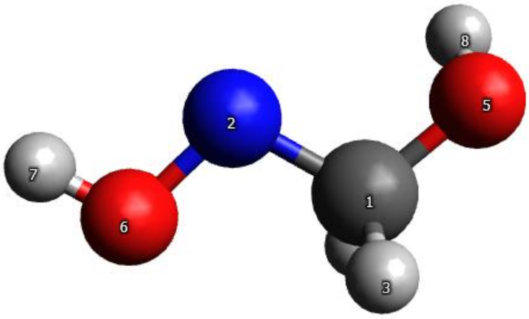

Figure 4. The final structure of the OHCH2NOH molecule in the fourth reaction.

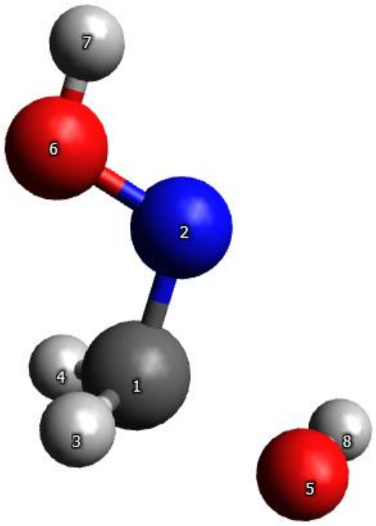

Figure 5. The final structure in the fifth reaction.

3. Conclusions

As a result of the study, it was found that the photoreduction of triplet nitromethane in the presence of dimethylamine proceeds through a sequence of well-defined stages with the formation of intermediates.

The key discovery was the identification of a five-stage process mechanism, where each stage is characterized by its own energy parameters. It has been established that the reaction is possible exclusively for aliphatic nitro compounds due to the presence of alpha-hydrogen.

An important result is the clarification of the mechanism of hydroxyl group separation, which occurs not directly from the nitrogen atom, but through the intermediate formation of a hydroxyl group in the methyl group. The critical values of the activation energy for the key stages are determined: 6.5 kcal/mol for the first stage, 22.9 kcal/mol for the second and 11.94 kcal/mol for the third, while the final stages proceed without an energy barrier.

The developed mechanism significantly complements the existing understanding of the processes of photo-reduction of nitro compounds and opens up new prospects for optimizing synthetic processes in organic chemistry. The results obtained are of fundamental importance for understanding the photochemical transformations of aliphatic nitro compounds and can be used to develop new methods for the synthesis of organic compounds.

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