One-Step Mechanism of Hydrogen Transfer in Amine—Triplet Nitro Compound System [†]

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Abstract: nitro compounds in the triplet state are strong oxidizing agents, one of the reactions of which is the excited-state hydrogen atom transfer. The energy characteristics of the reaction of triplet nitromethane with methylamine are obtained using *ab-initio* methods. MP2 and CASSCF methods were used. Calculated atomic charges has shown that the transfer of a proton must be accompanied by a simultaneous transfer of an electron. Optimization of the reaction complexes showed that in the course of the reaction there is a change in the reaction coordinate. The first stage is a rotation of methylamine molecule and the second stage is a lengthening of the C-H bond. Energetic and geometric parameters calculated by the MP2 and CASSCF methods are very close to each other which means the possibility of using the MP2 method for modeling similar processes as the main one.

Keywords: nitro compound; triplet state; hydrogen abstraction; quantum chemistry; electron transfer; bader theory

1. Introduction

Due to the close arrangement of the singlet and triplet electronic levels in the nitro compounds (NC), the intersystem crossing (ISC) probability increases significantly compared with other organic compounds [1]. It is known that the quantum yield of the triplet state in NB reaches 0.67 [2]. Such tendency is typical for all NC: both aliphatic and aromatic [2,3]. The chemical reactivity of triplet NC differs with singlet ones. They are able to transfer hydrogen from various compounds, including alcohols and amines [4–7].

The mechanism of hydrogen abstraction from amine has been insufficiently developed. It is reported that the process has a purely radical mechanism and proceeds according to the following scheme [8]:

1. $RNO_2 \leftrightarrows {}^1RNO_2^* \leftrightarrows {}^3RNO_2$
2. ${}^3RNO_2 + HM \leftrightarrows {}^3\{RNO_2 \cdots HM\} \leftrightarrows {}^3\{RN^\bullet O_2H \cdots {}^\bullet M\}$
3. ${}^3\{RN^\bullet O_2H \cdots {}^\bullet M\} \leftrightarrows RN^\bullet O_2H + M^\bullet$
4. $RN^\bullet O_2H + HM \leftrightarrows RN(OH)_2 + M^\bullet$
5. $RN(OH)_2 \leftrightarrows RNO + H_2O$

The first equation presents the NC internal conversion followed by ISC. Excited NC able to react with hydrogen donor, HM. After *pre*-reaction complex formation hydrogen transfer takes place. Intermolecular bond rupture leads to radical pair $RN^\bullet O_2H + {}^\bullet M$. Obviously, the reverse reaction is difficult due to the antiparallel spin orientation. The following process takes place after NC gains the second hydrogen atom. $RN(OH)_2$ is unstable compound and decays into nitroso compound and water molecule. We decide to investigate this process, especially the second reaction with hydrogen transfer.

Alternatively, the ionic mechanism may take place. The suggested process proceeds as following scheme [9]:

1. $RNO_2 \leftrightarrows {}^1RNO_2^* \leftrightarrows {}^3RNO_2$
2. ${}^3RNO_2 + HM \leftrightarrows {}^3\{RNO_2 \cdots HM\} \leftrightarrows {}^3\{RN^{\bullet-} O_2 \cdots HM^+\}$
3. ${}^3\{RN^{\bullet-} O_2 \cdots HM^+\} \leftrightarrows RN^{\bullet-} O_2 + HM^+$
4. $RN^{\bullet-} O_2 + H^+ \leftrightarrows RN^{\bullet}O_2H$
5. $RN^{\bullet}O_2H + HM \leftrightarrows RN(OH)_2 + M^{\bullet}$
6. $RN(OH)_2 \leftrightarrows RNO + H_2O$

The first equation is same as before, but on the second stage electron transfer takes place. NC ion-radical $RN^{\bullet-} O_2$ adds proton H^+ and then reactions 3 and 4 from the previous scheme are implemented.

It is known that the reaction can proceed in benzene or acetonitrile, where the ionic mechanism is less probable than the radical one [9]. Real-time TDDFT [10] calculations reveals that electron transfer between triplet NC and H_2S could not implemented. Theoretical investigations in this case are very efficient. Unfortunately, in hydrogen transfer reactions some of the DFT functionals are not trusted [11]: they predict negative energetic barriers of process. That numbers seems to contradict transition state theory. In recent article we pointed it out with B3LYP functional [12]. It was also found that the interaction of excited NC with amine is rather complex and the method is preferable for such calculations. It is also possible to use double-hybrid DFT functionals, e.g., B2PLYP [13]. When simulating NC in the triplet state, there is a significant spin contamination that can which can be reduced by applying the orbital space optimization procedure.

Present work considers the triplet NC with amines interaction. Radical mechanism of hydrogen transfer from amine methyl group would be discussed.

2. Methods

OMP2 and CASSCF quantum chemistry methods are applied to calculations. GAMESS [14] software packages provided Möller-Plesset method with orbital space optimization procedure. OpenMolcas [15] implementation of CASSCF was also used.

OMP2 method may be applied to excited systems in the ground triplet state, so we have decided to use it in our calculations. It also needs some verification on target system. The thermodinamics and spectroscopic data may be compared with other methods or experimental data. In Table 1 the calculated enthalpy changes of the reaction of triplet HNO_2 and NH_3, PH_3, AsH_3 are presented. HNO_2 molecule was selected as simplest nitro compound. Simplification is needed as CCSD(T) is intense method. In all cases the temperature and pressure conditions are set to 298.15 K and 1 atm. All DFT, OMP2 and CC calculation provided by Psi4 software [16]. CCSD(T)/cc-pVDZ method is known as "golden standard" for thermodinamics investigations and its results we using for comparision. In cases of PH_3 and AsH_3 OMP2 one has the best accordance to CC. B3LYP and CAM-B3LYP has better suitability than OMP2 in case of NH_3 reaction.

Table 1. Enthalpy changes of the reaction of triplet HNO_2 with listed molecules, units are in $kcal \cdot mol^{-1}$.

Reactant	B3LYP	OMP2	CAM−B3LYP	B2PLYP	CCSD(T)
NH_3	1.90	5.06	−1.33	−6.44	0.72
PH_3	−20.37	−21.44	−24.79	−28.77	−21.79
AsH_3	−26.34	−26.96	−30.84	−30.61	−27.33

Nitromethane molecule IR spectrum was choosen for spectroscopic data comparision. In Table 2 calculated frequencies and experimental frequencies are listed. The scale factor is applied in order to reduce anharmonicity. All calculations of frequencies are based on harmonic approximation and

it is needed to apply the scale factor. OMP2 has the better accordance with experiment in mid-numbers area, unless B3LYP shows more accurate results with low-numbers.

Table 2. Calculated and experimental IR frequencies of nitromethane comparision. Units are in cm^{-1}.

B3LYP	B2PLYP	OMP2	Experiment [1]
473	460	442	475
588	582	541	603
646	643	609	657
898	895	824	918
1062	1060	1028	1096
1078	1084	1060	1131
1336	1340	1217	1380
1380	1362	1322	1397
1385	1399	1355	1410
1401	1411	1400	1434
1625	1601	1413	1583
2957	2990	2959	2976
3065	3094	3074	3045
3096	3123	3094	3080
Scale factor			
0.9707	0.9621	0.9464	-

1—D Gorse, D Cavagnat, M Pesquer, C Lapouge "Theoretical and spectroscopic study of asymmetric methyl rotor dynamics in gaseous partially deuterated nitromethanes" J. Phys. Chem. 97(17) 4262-4269, 1993

Holding in mind our previous article that presents negative energetic barriers calculated with B3LYP we considered to adopt OMP2 methodology as main. Moreover our investigations revealed that cc-pVDZ basis set is not applicable to hydrogen transfer between methyl group and NC. Pople's 6-31g(d,p) basis set adopted. With Dunning basis the energy of SCF procedure diverges.

CASSCF (Complete Active Space in Self-Consisted Field) method adopted for excited molecules calculations. For accurate results it takes a set of orbitals and electrons. We might select the orbitals by its form investigation. As the main process carries the bond rupture and excited state, the selection must be done for the next orbitals:

- σ-bond for hydrogen transfer
- n-orbitals of NC
- π-system of NC

10 electrons on 8 orbitals are selected for active space. All pictures are presented in supplemental materials.

3. Discussion

3.1. Hydrogen Transfer

3.1.1. Geometry and Charges

On Figure 1 *post*-reaction complex for hydrogen transfer reaction between methylamine and nitromethane is given. This structure obtained using OMP2/6-31g(d,p) method. Numbers next to

bonds denote their length, and numbers next to atoms indicate their charge. All charges are calculated by Bader's method. It would be useful to compare the atomic charges with individual molecules. In Table 3 Bader's charges (q) and spin densities (ϱ) of nitromethane atoms are given for singlet and triplet states. Obviously, in the singlet state all spin densities are zeros, but in the triplet state electrons tends to locate next to nitro group. So, nitro compound in the triplet state may act as biradical. Charge values are given as q. As we can see, oxygen atoms charges are slightly higher in the triplet state rather than in the singlet state. Nitrogen charge is dramatically lower in the triplet state compared with singlet one.
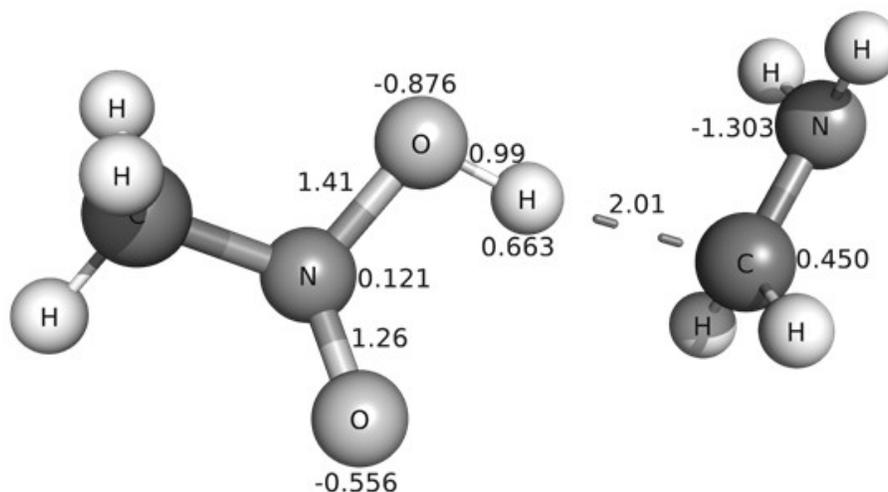

Figure 1. *Post*-reaction complex for the reaction of hydrogen transfer in the triplet nitromethane and methylamine system. Numbers next to atoms denote Bader's atomic charges (in a.u.), numbers next to bonds denote their lengths (in Angstroms).

Table 3. Atomic charges (q, a.u.) and spin densities (ϱ) of nitromethane molecule in the singlet and triplet states.

Atom	Singlet		Triplet	
	q	ϱ	q	ϱ
O1	−0.468	0.000	−0.333	0.151
O2	−0.471	0.000	−0.333	0.151
N	0.480	0.000	0.193	0.235
C	0.283	0.000	0.348	0.024
H	0.061	0.000	0.041	0.001

Atomic charges of oxygen atoms in individual molecule compared with *post*-reaction complex shown on Figure 1 are dramatically different. Charge of atom changes more than two times relative to individual molecule. Such behavior indicates that oxygen atom tights the electron density of the hydrogen atom. It seems that the reaction accompanied by charge transfer. Consequently, the mechanism of the reaction must be radical.

Considering the bond length in the complex shown on Figure 1 we can see that one of the oxygen atoms is more distant from nitrogen atom than second one. One of the bonds is of 1.26 Å and second one is of 1.41 Å between oxygen and nitrogen atoms. It means double-bonded and single-bonded atoms. Note that charge value of nitrogen atom changes slightly compared with

individual molecule. The distance between two molecules is of 2.01 Å, which means the presence of hydrogen bond. Using Bader's Atom in Molecules (AIM) theory, the critical point type (3, -1) was found between C and H atoms. Despite the fact that the theory cannot classify bond types, we believe that interaction between molecules may be assigned to hydrogen bonding. Analogous interactions we observed between amino group and NC in previous article [13].

3.1.2 Mechanism and Energies

Consider the mechanism of the hydrogen atom transfer. The *pre*-reaction complex for nitromethane—methylamine system cannot be found so the part of potential energy surface (PES) for the hydrogen transfer was obtained with constrained optimization. Figure 2 presents the intrinsic reaction coordinate graph for hydrogen transfer calculated using OMP2 method. On horizontal axis the C-H bond length presented.
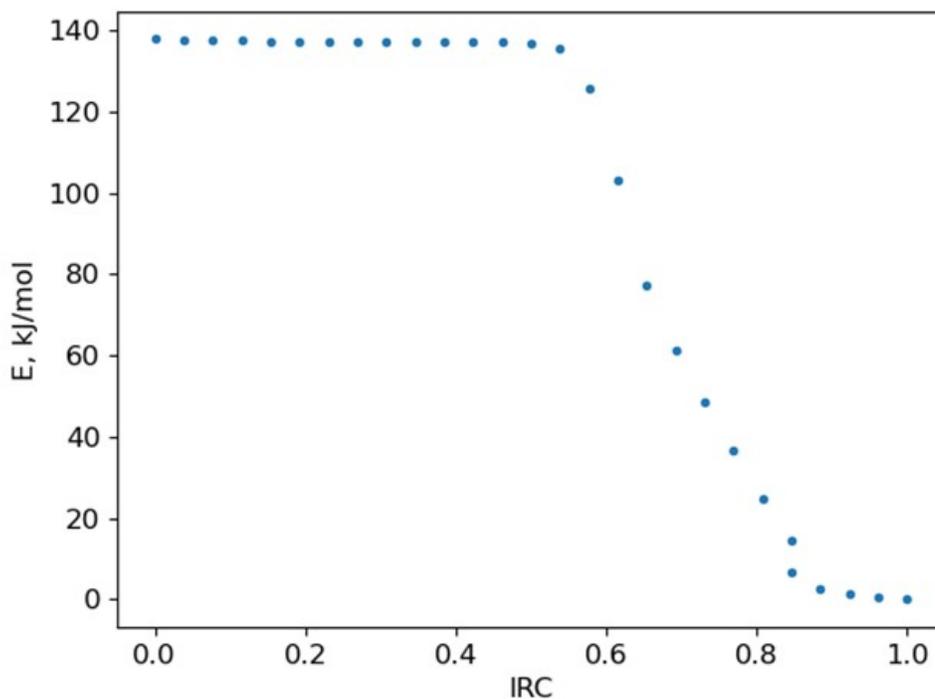

Figure 2. Intrinsic reaction coordinate graph for hydrogen transfer reaction between triplet nitromethane and methylamine calculated using OMP2/6-31g(d,p) method.

Plateau on the graph's left side assigned to bonded molecules. Energy difference between isolated molecules and bonded radical pair consists 137.9 kJ·mol^{-1}. Inspecting the curve we may see that there is no transition state or *pre*-reaction complex points. Optimizing structure of bonded molecules we located a minimal structure presented on the Figure 3. Reaction coordinate change takes place. The first step is methylamine molecule rotation from structure shown on Figure 3 and the second step is hydrogen transfer. Oxygen atoms charges are higher than on the Figure 1; the intermolecular distance is of 2.69 Å. So we may conclude that hydrogen atom transfer takes place in this reaction.
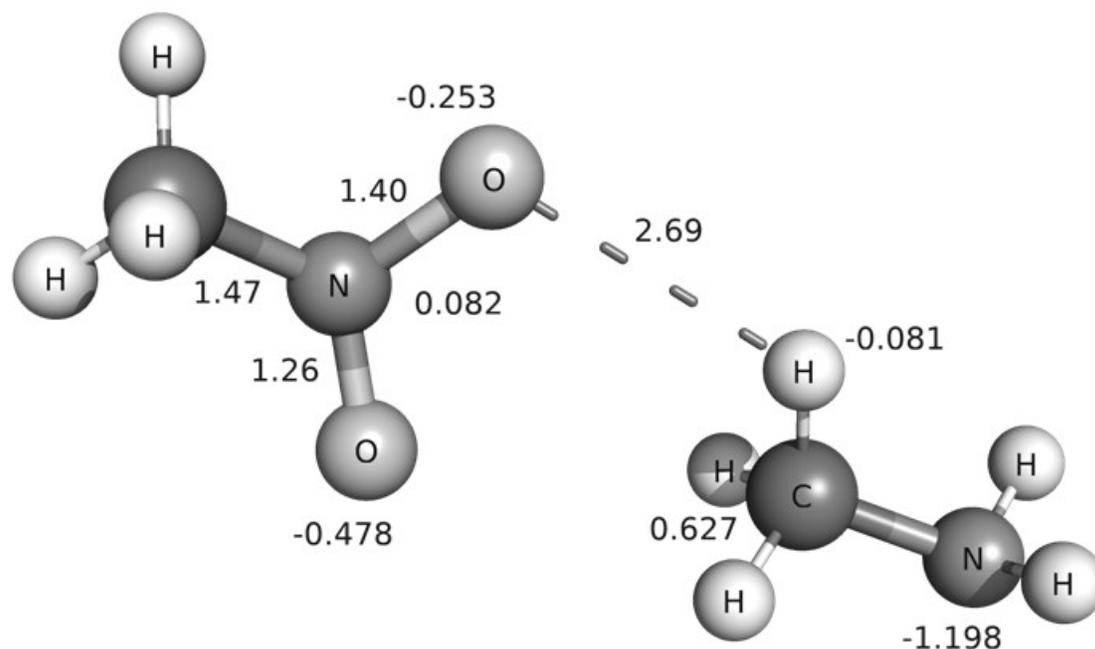
Figure 3. *Pre*-reaction complex of triplet nitromethane and methylamine hydrogen transfer reaction.

CASSCF(10,8)/6-31g* method selected for OMP2 results verification. Using the constrained optimization procedure the same graph, as on the Figure 2, was obtained. Energy difference is of 135.7 kJ·mol⁻¹. That value very close to OMP2/6-31g(d,p) calculated energy. We may conclude that OMP2 method is applicable for this reaction investigation.

4. Conclusions

The photochemical hydrogen abstraction reaction investigated using quantum chemistry methods. The process of hydrogen transfer between triplet nitromethane and methyl group of methylamine was the point of interest. We stated that reaction proceeds trough reaction coordinate change. *Pre*-reaction complex formation and methylamine rotation is a first step. The second step is hydrogen atom abstraction trough C-H bond rupture. That two steps are the one elementary reaction. Calculated energy difference of hydrogen atom transfer is of 137.9 kJ·mol⁻¹.

References

1. Giussani, A.; Worth, G.A. Insights into the Complex Photophysics and Photochemistry of the Simplest Nitroaromatic Compound: A CASPT2//CASSCF Study on Nitrobenzene. *J. Chem. Theory Comput.* **2017**, *13*, 2777–2788, doi:10.1021/acs.jctc.6b01149.
2. Hurley, R.; Testa, A.C. Triplet-state yield of aromatic nitro compounds. *J. Am. Chem. Soc.* **1968**, *90*, 1949–1952, doi:10.1021/ja01010a004.
3. Arenas, J.F.; Otero, J.C.; Peláez, D.; Soto, J. Role of surface crossings in the photochemistry of nitromethane. *J. Chem. Phys.* **2005**, *122*, 84324, doi:10.1063/1.1851977.
4. Trotter, W.; Testa, A.C. Photoreduction of aromatic nitro compounds by tri-n-butylstannane. *J. Am. Chem. Soc.* **1968**, *90*, 7044–7046, doi:10.1021/ja01027a028.
5. Hashimoto, S.; Kano, K. The Photochemical Reduction of Nitrobenzene and Its Reduction Intermediates. X. The Photochemical Reduction of the Monosubstituted Nitrobenzenes in 2-Propanol. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 549–553, doi:10.1246/bcsj.45.549.

2. Cohen, S.G.; Parola, A.; Parsons, J.G.H. Photoreduction by amines. *Chem. Rev.* **1973**, *73*, 141–161, doi:10.1021/cr60282a004.

3. Ayscough, P.; Sealy, R. A photochemical application of kinetic electron spin resonance: Rates of hydrogen abstraction by triplet state carbonyl compounds. *J. Photochem.* **1972**, *1*, 83–85, doi:10.1016/0047-2670(72)80008-x.

4. El Latif, F.A.; Barsy, M.; Rady, E.; Hassan, M.; El Maghraby, M. Photoinduced reaction of polyfunctional nitroaromatics: Photoreduction versus photosubstitution reaction of nitrobenzylidene malonic derivatives with triethylamine. *J. Photochem. Photobiol. A Chem.* **1999**, *121*, 111–117, doi:10.1016/s1010-6030(98)00413-4.

5. Görner, H. Oxygen uptake after electron transfer from donors to the triplet state of nitronaphthalenes and dinitroaromatic compounds. *J. Photochem. Photobiol. A: Chem.* **2008**, *195*, 235–241, doi:10.1016/j.jphotochem.2007.10.007.

6. Fomichev, D.A.; Ovsyannikov, D.V.; Zelentsov, S.V. Study of Charge Transfer in Radical Reactions of Hydrogen Atom Detachment Involving Triplet Nitro Compounds. *High Energy Chem.* **2020**, *54*, 254–258, doi:10.1134/s0018143920040050.

7. Tishchenko, O.; Truhlar, D.G. Benchmark Ab Initio Calculations of the Barrier Height and Transition-State Geometry for Hydrogen Abstraction from a Phenolic Antioxidant by a Peroxy Radical and Its Use to Assess the Performance of Density Functionals. *J. Phys. Chem. Lett.* **2012**, *3*, 2834–2839, doi:10.1021/jz3011817.

8. Ovsyannikov, D.; Zelentsov, S.V. Reactivity of Aliphatic and Aromatic Nitrocompounds in the Triplet State with Respect to Amines. *Russ. J. Phys. Chem. A* **2020**, *94*, 1603–1606, doi:10.1134/s0036024420080221.

9. Ovsyannikov, D.V.; Zelentsov, S.V. Role of Complexation between Monomethylamine and Triplet Nitromethane Molecules in the Hydrogen Transfer Reaction. *High Energy Chem.* **2019**, *53*, 103–107, doi:10.1134/s0018143919020139.

10. Barca, G.M.J.; Bertoni, C.; Carrington, L.; Datta, D.; De Silva, N.; Deustua, J.E.; Fedorov, D.G.; Gour, J.R.; Gunina, A.O.; Guidez, E.; et al. Recent developments in the general atomic and molecular electronic structure system. *J. Chem. Phys.* **2020**, *152*, 154102, doi:10.1063/5.0005188.

11. Galván, I.F.; Vacher, M.; Alavi, A.; Angeli, C.; Aquilante, F.; Autschbach, J.; Bao, J.J.; Bokarev, S.I.; Bogdanov, N.A.; Carlson, R.K.; et al. OpenMolcas: From Source Code to Insight. *J. Chem. Theory Comput.* **2019**, *15*, 5925–5964, doi:10.1021/acs.jctc.9b00532.

12. Parrish, R.M.; Burns, L.A.; Smith, D.G.A.; Simmonett, A.; DePrince, A.E.; Hohenstein, E.G.; Bozkaya, U.; Sokolov, A.Y.; Di Remigio, R.; Richard, R.M.; et al. Psi4 1.1: An Open-Source Electronic Structure Program Emphasizing Automation, Advanced Libraries, and Interoperability. *J. Chem. Theory Comput.* **2017**, *13*, 3185–3197, doi:10.1021/acs.jctc.7b00174.