Comparison of complex formation mechanisms in hydrogen abstraction reaction between the nitro compound and ammonia

Dmitriy Ovsyannikov *, Vadim Laschonov
Lobachevsky State University of Nizhni Novgorod
Correspondence: ovsyannikov@chem.unn.ru

Abstract: Present work aimes to compare two possible pathways of a pre-reaction complex in the reaction of transfer of a hydrogen atom from ammonia to a nitro compound forming. Nitrobenzene, nitromethane and HNO_2 were used as nitro compounds. The proposed paths are: nitro compound intersystem crossing with a subsequent search for a substrate or the formation of a complex with its subsequent excitation. The calculations were performed using TDPBE0/TDA/ aug-cc-pVDZ method in NWChem-6.8 program. In verification purposes, some additional calculations were performed using RASCI/aug-cc-pVDZ method in PSI4 program. The location of the levels and the geomety of the complexes shows that the triplet complex (exciplex) is more stable than the singlet complex. The weak coupling between molecules in the singlet complex indicates that the probability of its excitation is very small. Moreover, there are experimental data, where the quantum yields of such reactions reaches 0.3. The presented calculations confirm the mechanism of the nitro compound intersystem crossing with a subsequent search for a substrate.

Keywords: photoreduction, amines, nitrocompound, excited state, hydrogen abstraction, photochemistry, quantum chemistry

Introduction

Hydrogen transfer reactions involving excited nitro-compounds have been studied for a long time. It is known that in the triplet state, aromatic nitro-compounds are able to hydrogen atom from amines and ketones abstraction [1], [2]. For example, according to the scheme

$$^3\left(ArNO_2\right)+\left(CH_3\right)_2CHOH \rightarrow Ar\dot{N}O_2H+\left(CH_3\right)_2\dot{C}OH \, , \qquad (1)$$
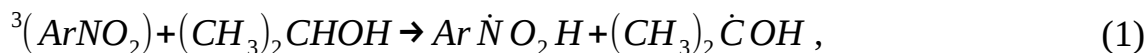
the triplet nitro-compound reacts with alcohol and yields the radical pair. The mechanism of such a reaction is complicated. It may include direct or sensitized photoexcitation. These may be dark radical processes, or occur under the action of light. Initial electron transfer with the yield of ion-radicals is possible.

It has been established that in an air-saturated atmosphere the quantum yield of the hydrogen transfer reaction drops sharply [3]. This suggests participation in the reaction of triplet particles.

The current work aims to compare the possibility of forming a pre-reaction complex of different multiplicities. It is expected the formation of a strong-bonded complex between reactants. Then, a

photoexcitation takes place, followed by an intersystem transition. An alternative mechanism is the initial excitation of the nitro compound with the subsequent formation of a pre-reaction complex.

Methodology

The formation energy comparision of the pre-reaction complex between nitrocompound and substrate was performed. The model systems are:

$$\{HNO_2 + NH_3\} \tag{2}$$

$$\{CH_3NO_2 + NH_3\} \tag{3}$$

$$\{PhNO_2 + NH_3\} \tag{4}$$

All systems are calculated using TDPBE0/aug-cc-pVDZ time-depended hybrid functional. NWChem-6.8 [4] for this purposes was used. Table 1 summarizes the geometry parameters of CH_3NO_2 in singlet state for some DFT functionals. TDPBE0 with aug-cc-pVDZ basis set is acceptable for current molecule.

Table 1.

CH_3NO_2 in singlet state geometry comparision

Parameter	TDPBE0/aug-cc-pVDZ	M06-2X/aug-cc-pVTZ [1]	B3PW91/6-31g(2df,p) [1]	Experimental [2]
r(C-H) *	1.092	1.083	1.088	1.088
r(C-N)*	1.486	1.492	1.492	1.489
r(N-O) *	1.215	1.206	1.216	1.224
a(H-C-N) **	106.5	106.7	106.8	107.2
a(O-N-O) **	125.6	124.5	126.1	125.3

* r – distance between atoms, Å
** a – valence angle, degrees
1 https://cccbdb.nist.gov
2 Hellwege K.H., Hellwege A.M. (ed.). Landolt-Bornstein: Group II: Atomic and Molecular Physics Volume 7: Structure Data of Free Polyatomic Molecules. Springer-Verlag. Berlin. 1976.

Some of the calculations were performed using RASCI/aug-cc-pVDZ [5] method. PSI4 [6] program was used. For (3) complexes on ground triplet-state active space contains: RAS1 – 6 orbitals, RAS2 – 3 orbitals, RAS3 – 3 orbitals, RAS4 – 6 orbitals with total 18 electrons on 18 orbitals. The arbitrary calculation using RASSCF(4,4,4)/cc-

pVDZ for (3) complex was performed. On singlet-state complex the next natural orbital (NO) occupation numbers were recieved:

A 1.990012   A 1.989464   A 1.979117

A 1.976980   A 1.975171   A 1.892838

A 0.129193   A 0.029386   A 0.018901

A 0.010374   A 0.007504   A 0.001060

Letter A means orbital symmetry. The C_1 point group is used so all orbitals have the same symmetry. One HONO and 3 LUNO are with low contributions and may be neglected in calculations. As expected, the similar singlet-state can not be described with one-determinant wavefunction. The most important determinants are:

* 1 -0.950525 (0,   0) 16AX 17AX 18AX 19AX 20AX 21AX

* 2   0.201064 (2,   2) 16AX 17AX 18AX 19AX 21AX 22AX

This distribution indicates that one-determinant methods are not reliable for current systems. So comparision with multi-determinant methods required.

PSI4 provides Symmetry Adapted Perturbation Theory (SAPT) [7] which may be used to calculate intermolecular coupling energy. The aug-cc-pVDZ basis set and SAPT0 theory level was used.

Results and Discussion

Table 2 summarizes formation energies of (2), (3) and (4) complexes in singlet and triplet states. ${}^3\{$ $PhNO_2$ + NH_3 $\}$ PBE0 energy was obtained using PSI4 program. Formation energy is calculated as difference between energy of complex and sum of separated molecules energies. It is seen that SAPT0 gives formation energy 1.2-1.8 times higher than TDDFT. SAPT on higher levels of theory can give lower energy. But SAPT2 and higher are not available for unrestricted wavefunctions. For triplet-state (3) complex RASCI gives 7.46 kJ·mol^{-1}. These energies are very close to each other for singlet-state and triplet-state complexes.

Picture 1 demostrates the singlet and triplet (2) complex. HNO_2 geometry depends on multiplicity. In the singlet state four atoms are lying in one plane. In the triplet state H-atom lies not in N-O-O plane.

Table 2.

Complex formation energies comparision

RNO$_2$ R =	Singlet		Triplet	
	TDPBE0, kJ·mol^{-1}	SAPT0, kJ·mol^{-1}	TDPBE0, kJ·mol^{-1}	SAPT0, kJ·mol^{-1}
H	-4.41	-7.81	-5.06	-9.39
CH$_3$	-7.04	-9.18	-6.35	-10.18
Ph	-7.97	-10.18	-5.21	-12.70

a)   b)
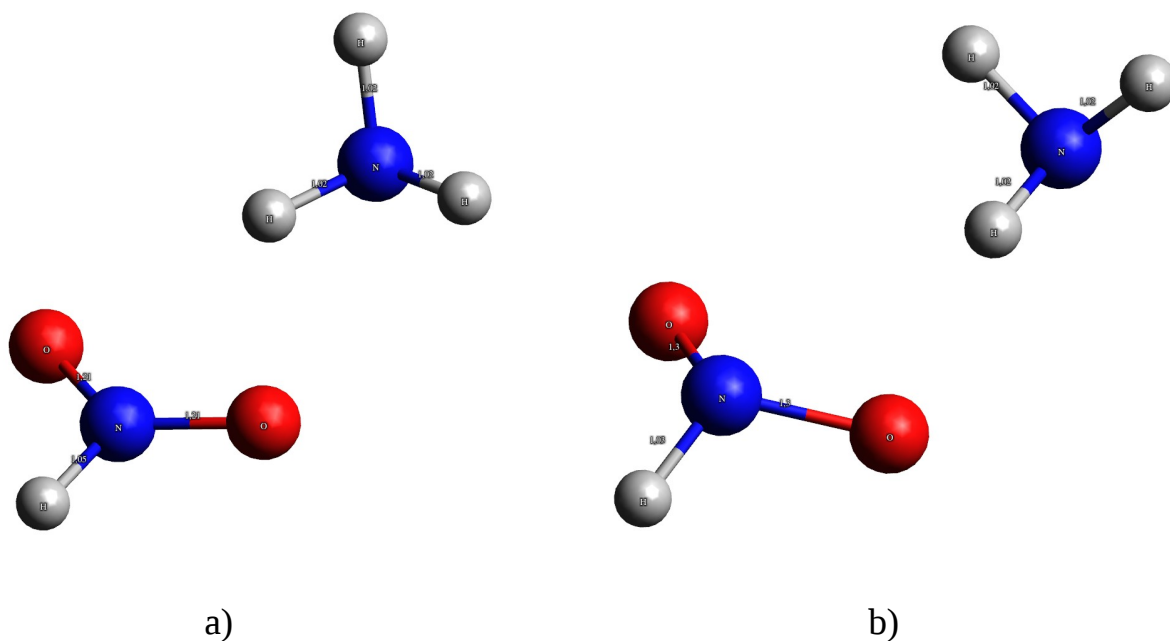
Picture 1. *HNO$_2$ + NH$_3$ geometry in a) singlet b) triplet state*

Conclusions

Comparing the formation energies of complexes between nitro compounds and ammonia we concluded that there is no significant difference between singlet-state and triplet-state complexes. Evidently, weak-coupled, both of them cannot exist for long time. An immediate exposure of light on the singlet-state complex or the initially excited into triplet manifold nitro compound needed. So it may be concluded that initial triplet state complex is the preferable reaction pathway.

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