CHEMISTRY OF NITROSAMINE: A QMC STUDY OF THERMAL De-NOx PROCESS

Francesco Fracchia[a], Claudio Amovilli[a] and Claudia Filippi[b]
[a]Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Pisa, Italia
[b]University of Twente, Faculty of Science and Technology and MESA+ Research Institute, Enschede, The Nederlands

ABSTRACT

The potential energy surface for the NH_2 + NO reaction has been characterized by determining the critical point geometries at the QCISD/6-311++G** level of the theory and the corresponding energies by means of the QMC methodologies. The aforementioned reaction is important to the understanding of the so called thermal deNOx process, a chemical treatment used in stationary combustion systems to control emission of nitrogen oxides [1]. Similar reactions are also involved in atmospheric chemistry [2]. The commonly accepted mechanism for this process involves the formation of nitrosamine (NH_2NO) and its tautomers as intermediates and leads to water and nitrogen as final products. An alternative reactive channel brings to the species N_2H and OH. This channel is energetically less favorable but it is important because is chain branching whereas the first is chain terminating. In fact N_2H and OH contribute to reformation of NH_2 allowing the self-sustaining of the main process. A further channel to $N_2O + H_2$ could be considered, in principle, but the saddle point in the corresponding path lies to high in energy to be kinetically significant. We have studied both the two most important processes finding four transition states for the main path plus other two of a secondary path and the geometries of all intermediates. In order to account for all chemical bond rearrangements, we used an appropriate multireference wave function which included the most important configurations extracted from a CASSCF wave function. The QMC calculations have been performed at both VMC and FN-DMC level and multiplying the above multideterminantal part by a Jastrow factor including electron-nucleus, electron-electron and electron-electron-nucleus many body terms. Specific VDZ Gaussian basis sets [3] and pseudopotentials [4] have been used for all atoms. For the quantum chemistry calculations we used the standard packages Gaussian 03 and Gamess while for the QMC part of this work we used the CHAMP code [5]. Our computed barrier heights and reaction energies fall in the range of data of the most accurate theoretical works found in the literature [2, 6-8], including also DFT calculations, and should be considered among the best for the quality of the electronic wave function used at the QMC level.

THE De-NOx PROCESS

Thermal De-NOx was developed by Richard Lyon at Exxon in the early 1970s [9]. It is an after-treatment scheme used on stationary combustion system at atmospheric pressure to control NO_x emission. The process is a selective, non-catalytic, gas-phase reaction employing ammonia as an additive. The reaction requires oxygen and occurs at a temperature ranging between 1100 and 1400 K. In the presence of water (i.e. in normal combustion products) ammonia is converted to NH_2 by reaction with hydroxyl

$NH_3 + OH \rightarrow NH_2 + H_2O$

The NH_2 radical reacts with NO proceeding through two primary channels:

$NH_2 + NO \rightarrow N_2 + H_2O$

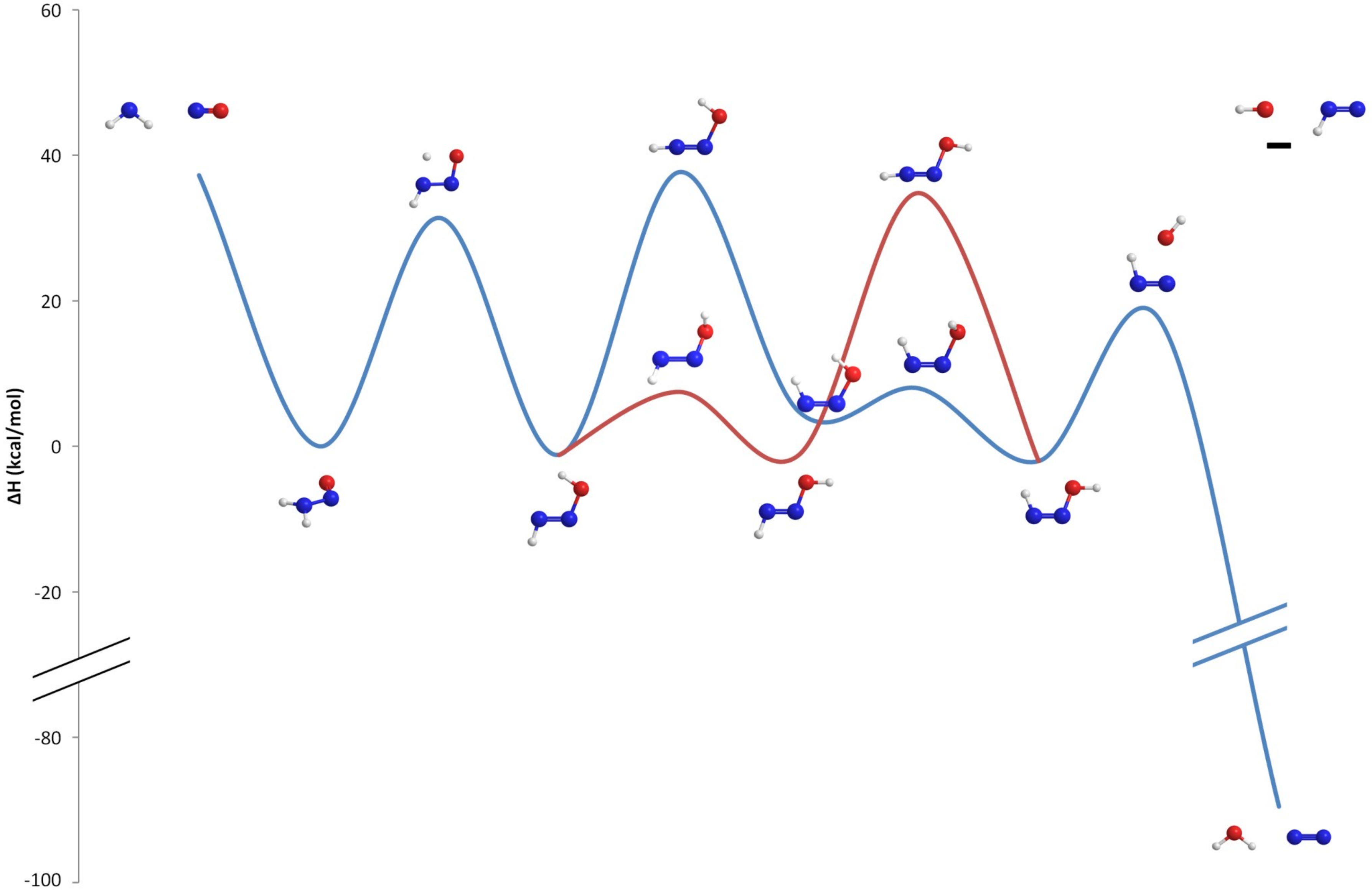
$NH_2 + NO \rightarrow N_2H + OH$

The second channel must constitute at least 25% of the total reaction to obtain a self-sustaining process. Infact a hydrogen atom formed from N_2H leads to three OH radicals in the presence of O_2:

$H + O_2 \rightarrow OH + O$

$O + H_2O \rightarrow OH + OH$

The second channel thus provides four OH groups for every OH consumed, and each of the hydroxyl produced can then give a NH_2 radical.


60
40
20
0
-20
-80
-100
ΔH (kcal/mol)

METHOD

CASSCF $$\Phi = \sum_{k}^{ALL\ CSFs} c_k D_k^{\uparrow} D_k^{\downarrow}$$

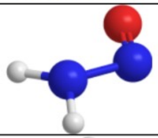
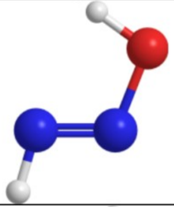
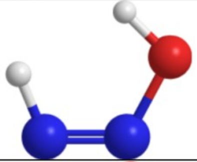
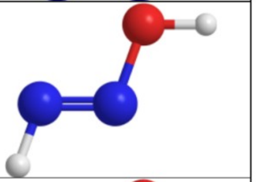
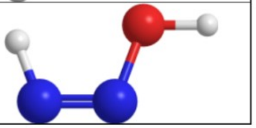
QMC $$\Psi = \sum_{k}^{SELECTED\ CSFs^*} d_k D_k^{\uparrow} D_k^{\downarrow} J(r_{ij}, r_{iA})$$

VMC Optimization of d_k and J by energy minimization

FN-DMC

*Selection of CSFs according to $\sum_k |c_k|^2 \geq 0.97$

LEGENDA

Geometry	Point group	Structure
M1	C1	
M2	Cs	
M3	Cs	
M4	Cs	
M5	Cs	

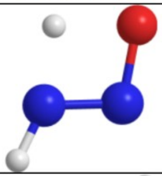
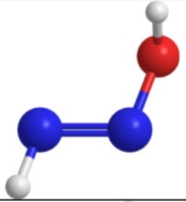
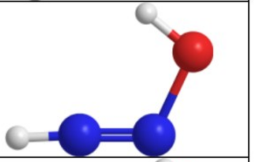
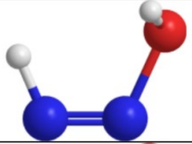
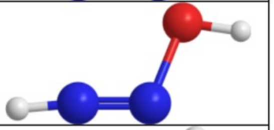
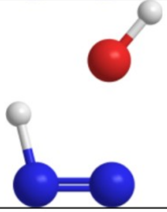
Geometry	Point group	Structure
TS1	Cs	
TS2	C1	
TS3	C1	
TS4	C1	
TS5	C1	
TS6	Cs	

TABLE I. Trial functions employed

Species	CAS	N determinants
NH_2	(5,4)	6
NO	(11,8)	48
M1	(16,12)	181
TS1	(16,12)	166
M2	(16,12)	113
M3	(16,12)	137
M4	(16,12)	124
M5	(16,12)	112
TS2	(16,12)	173
TS3	(16,12)	128
TS4	(16,12)	169
TS5	(16,12)	123
TS6	(16,12)	121
H_2O	(6,4)	6
N_2	(10,8)	80
OH	(5,3)	1
N_2H	(11,9)	180

TABLE II. Relative energies of reactants, products, intermediates, and transition states for the NH_2 + NO reaction at various levels of theory[a]

		Present work[c]						
Species	ZPE[b]	VMC	DMC	CCSD(T)[d]	G2M[e]	B3LYP[e]	PMP4[e]	CASPT2[f]
NH_2 + NO	14.6	33.2	37.2	41.7	46.7	44.2	38.3	42.8
M1	20.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TS1	17.6	32.3	31.4	29.6	31.9	31.6	29.6	28.4
M2	21.0	-1.1	-1.2	-1.8	0.1	1.5	0.5	-0.6
M3	20.2	5.2	4.7	4.5	6.5	7.7	6.9	
M4	21.1	-0.9	-1.1	-1.0	0.7	2.6	2.3	1.0
M5	20.6	-1.4	-2.0	-1.4	0.4	1.3	0.7	
TS2	20.3	8.1	7.5	8.3	8.9	11.2	10.5	
TS3	18.3	38.7	37.7	37.3	38.6	37.1	41.5	
TS4	19.8	9.7	8.0	7.7	9.3	11.2	10.4	
TS5	18.3	35.9	34.6	33.9	35.8	34.5	39.6	
TS6	16.5	17.5	17.6	19.6	21.8	24.3	22.0	
H_2O + N_2	16.7	-95.0	-89.5	-79.7	-77.6	-70.5	-79.4	
N_2H + OH	13.7	36.3	41.3	44.2	50.3	45.4	45.0	

[a] All energies are in units of kcal mol^{-1} including zero-point energy (ZPE) corrections.

[b] Zero-point energy corrections were calculated at the QCISD/6-311G(*d*,*p*)++ level of theory.

[c] Variances for VMC and DMC energies are 0.1 kcal mol^{-1}

[d] Ref. [7]

[e] Ref. [6]

[f] Ref. [8]

TABLE III. Comparison with DMC.

	Present work					
Species	VMC	CCSD(T)	G2M	B3LYP	PMP4	CASPT2
NH_2 + NO	-4.0	4.5	9.5	7.0	1.1	5.6
M1	0.0	0.0	0.0	0.0	0.0	0.0
TS1	0.9	-1.8	0.5	0.2	-1.8	-3.0
M2	0.1	-0.6	1.3	2.7	1.7	0.6
M3	0.5	-0.2	1.8	3.0	2.2	
M4	0.3	0.1	1.8	3.7	3.4	2.1
M5	0.6	0.6	2.4	3.3	2.7	
TS2	0.6	0.8	1.4	3.7	3.0	
TS3	1.1	-0.4	0.9	-0.6	3.8	
TS4	1.8	-0.3	1.3	3.2	2.4	
TS5	1.1	-0.9	1.0	-0.3	4.8	
TS6	0.0	2.1	4.3	6.8	4.5	
H_2O + N_2	-5.5	9.8	11.9	19.0	10.1	
N_2H + OH	-5.0	2.9	9.0	4.1	3.7	

COMPARISION WITH EXPERIMENTAL DATA

TABLE IV. ΔH (0 K) for reaction $NH_2 + NO \rightarrow H_2O + N_2$, in kcal/mol

	Present work					
Exp.[a]	VMC	DMC	CCSD(T)	G2M	B3LYP	PMP4
-123.93	-128.2	-126.7	-121.4	-124.3	-114.7	-117.7

[a] Ref. [10,11]

DISCUSSION

Data of Table III show a good agreement between CCSD(T) calculations and our QMC results for the minima and the saddle points of the schematic path depicted in the plot above. The discrepancies are smaller than the differences between the energies obtained by the other methods shown in the same table. Although the reaction energy for the global process is in substantial agreement with the unique experimental data, much larger differences have been found, instead, for all the three dissociative channels. Unfortunately, comparing all data of Table II is not sufficient to establish which of the methods is the most appropriate for the fragmentations. About this point, it should be noted that in Table II we have brought to coincidence the energies of nitrosamine (M1). For a deeper understanding of this problem, our study need to be completed by adding calculations performed with all different choices of fragment active spaces which are consistent with the M1 active space of 16 electrons in 12 orbitals. This work is actually in progress.

CONCLUSIONS

The de-NOx process illustrated here is a good example of a chemical reaction that proceeds along a complicate path through a series of intermediates and transition states. In such cases only *ab initio* methods of calculations can provide data that can be used to interpretate structural and kinetic aspects of the chemical reaction. The approach we used in this example, which combines the search of critical points of a PES by standard quantum chemistry methods and QMC for the evaluation of corresponding electronic energies, is shown to be reliable provided that an appropriate active space has been defined. The use of Jastrow factors allows the definition of a minimal active space which must include the orbitals involved in the overall electronic redistribution. In order to limit the number of Slater determinants we used a practical method of truncation based on the weight of CSFs in the source CASSCF wavefunction. This method could become critical for very large active space and will be reviewed in future applications on larger systems. In going from molecular aggregates to fragments (dissociative channels) there is the problem of balancing of the errors which arise from the different choices of fragment active spaces. The results shown in this poster seem to be unbalanced if compared with results from other methods. The complete analysis is under consideration. In principle the fragments can be treated at the deeper level but the limiting factor is that the aggregate active space must be constructed by the sum of the fragment active spaces, a procedure which becomes prohibitive very rapidly with the size of the molecules.

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