Budownictwo i Architektura 15(3) (2016) 75-81

Numerical methods in understanding reaction pathways NO_x oxidation

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Abstract: Different quantum chemical models were applied in energetic analysis of process of oxidation of NO and NO_2 through reaction with ozone generated by non-thermal equilibrium (low temperature), atmospheric pressure plasma. The potential energy surfaces of systems comprising NO and NO_2 with ozone were characterized. The NO_x oxidation processes well known, at the molecular level, were modelled by *ab initio* quantum methods to calculate the total reaction energy, E_t, of each step in the reaction chain. chemistry was further applied in an attempt to detect the presence of any transition states to calculate the activation energy, E_a, of reactions (1) NO + O_3 and (2) NO_2 + O_3 using the MP2 level of theory with three different basis sets and fine potential energy scan resolution.

Keywords: NO and NO_2, O_3, DFT; CASSCF; CCSD; MP2.

1. Introduction

Of interest to industry are techniques to destroy NO_x at the post-combustion, exhaust stage, commonly called end-of-pipe removal or abatement techniques? These include selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and plasma chemistry. SCR and SNCR techniques require substantial investment in equipment and have limitations in efficiency. These problems motivate development of an improved energy and chemicals efficient, widely applicable end-of-pipe NO_x abatement technology. Industrial plasma systems appears to offer technically feasible and commercially interesting solutions based on the Gas State conversion of NO_x into industrially useful by-products, such as nitric acid.

The overall oxidation process of NO_x by plasma generated ozone can be described by the following global reactions some or all of which reactions almost certainly incorporate intermediate stages in which intermediate species are generated:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (2)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (3)$$

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \quad (4)$$

The detailed mechanisms of these reactions are complex not well known, their understanding is key to making this method of NO_x conversion efficient and applicable in practice. One way to determine major factors which govern the process might be to perform exhaustive and expensive experimental studies but there would be no certainty that these

would reveal the important processes. An attractive alternative seems to be molecular modeling based on quantum chemical methods. Quantum chemistry today delivers very powerful tools for studying varied chemical problems.

We have applied quantum chemistry methods to describe the energetics of elementary reactions comprising the NO_x oxidation process. The modern theoretical techniques, involving the density functional theory (DFT) and *ab initio* multi-configurational approach (MCSCF), are well suited for this kind of calculation. We present our theoretical calculations of the total reaction energy, E_t, of each of steps (1) to (4) in the above reaction chain, in the detection of any transition states in each of the reactions and in calculation of the activation energy, E_a, of the initializing reactions (1) $NO + O_3$ and (2) $NO_2 + O_3$. This preliminary work aims at determining the relative thermodynamic probability of potentially competing reaction paths, e.g. (1) → (2) → (3) → versus (1) → (4)

2. Computational details and discussion

To investigate such oxidation processes, however, each reaction must be characterized at the molecular level and this was attempted using a total of five quantum chemical techniques:

1. Techniques to determine the total energy of reactions, E_t:
   a. Density Functional Theory (DFT) based Becke-3-Lee Yang Parr (B3LYP).
   b. Complete Active Space Self-Consistent Field (CASSCF).
2. Techniques to investigate transition states as work towards estimation of activation energies:
   a. Hartree Fock (HF).
   b. Moller Plesset Perturbation (MP2).
   c. Density Functional Theory (DFT) based Becke-3-Lee Yang Parr (B3LYP).
   d. Coupled Cluster with Singles and Doubles (CCSD) substitutions.

Techniques 1a and 1b above were applied in determination of the total reaction energy, defined as $E_t = E_{products} - E_{reactants}$, for reactions (1) – (4) above. The equilibrium geometries and electronic energies of substrates and products, namely the oxygen molecule, the ozone molecule, the mono-nitrogen oxide molecules, NO and NO_2 and the product molecules NO_3 and N_2O_5, were calculated as well as their zero-point vibration energy (ZPE). From these, total reaction energies corrected for the ZPE, E_t^{ZPE}, were also calculated.

DFT calculations were carried out using the parallel version of the Parallel Quantum Solutions quantum chemistry software [1] while the CASSCF calculations were carried out using the DALTON quantum chemistry software [2].

The calculations were done at the DFT/B3LYP/6-311G(d,p) and the CASSCF(σ-and π-derived)/6-31G(d,p) levels of theory. It was demonstrated that the DFT/B3LYP technique is superior to the *ab initio* CASSCF approach. The DFT method provides an efficient way of estimating the static and dynamic correlation energies for the strongly multi-configurationally species such as those considered in this work. Good agreement between the DFT/B3LYP and the experimental geometries as well as harmonic frequencies, where available experimentally, was achieved. In contrast, the CASSCF approach either tended to give the wrong structure of the molecule, e.g. the NO_3 molecule, or could not be applied due to computational problems, as for the N_2O_5 molecule. Accordingly, the ZPE corrected relative energies for reactions (1) – (4) above were computed at the DFT level only. The negative values of E_t^{ZPE} showed that energy was released and all the reactions are exothermic.

However, E_t alone is not sufficient to determine the relative probability of competing reaction paths. Only by determination of the complete energy scheme of each competing reaction path, including any critical intermediate or transmission reactions, and the energy changes for intermediate reactions, $\Delta E_i = E_{intermediates} - E_{reactants}$, can the relative thermodynamic probability of competing reactions be found. If we assume that the highest energy state of each of the reaction processes (1) to (4) is an intermediate state, then we can say that this defines the activation energy, E_a, of the particular reaction, i.e. $E_a \equiv \Delta E_i$. Four different quantum chemistry methods were, therefore, applied to try to determine the presence or absence of transitional or intermediate states. The methods partially characterized the potential energy surface computed as a function of the bond distance between the N-atom of the mono-nitrogen oxide (NO or NO_2) and the O-atom of ozone.

The 6-311g (d, p) 5d basis set level of theory was used in all four of the quantum chemical techniques.

2.1. Determination of total reaction energies, E_t

From application of the DFT and CASSCF methods described in previous work [4] the total reaction energies, defined as $E_t = E_{products} - E_{reactants}$, for the reactions (1) – (4) were determined by calculating the equilibrium geometries and electronic energies of substrates and final reaction products. These are the oxygen molecule, the ozone molecule and a few nitrogen oxide molecules NO_x, as well as their zero-point vibration energy (ZPE). Table 1 shows the total reaction energies, E_t, and the total reaction energies corrected for the zero point energy (ZPE), E_t^{ZPE}, for reactions (1) – (4) calculated at the DFT/B3LYP/6-311G(d,p) and the CASSCF(σ- and π-derived)/6-31G(d,p) levels of theory.

Table 1. Calculated total reaction energies, E_t, and total reaction energies corrected for the ZPE, E_t^{ZPE}, of reactions (1)-(4)

Reaction	Method	E_t [kcal/mol]	E_t^{ZPE} [kcal/mol]
$NO + O_3 \rightarrow NO + O_2$	DFT/B3LYP	-62.78	-62.31
	CASSCF	-31.36	-30.54
$NO_2 + O_3 \rightarrow NO_3 + O_2$	DFT/B3LYP	-37.56	-38.59
	CASSCF	-15.63	-14.69
$NO_2 + NO_3 \rightarrow N_2O_5$	DFT/B3LYP	-21.62	-16.90
	CASSCF	-	-
$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$	DFT/B3LYP	-59.18	-55.49
	CASSCF	-	-

2.2. Determination of activation energies, E_a

Reactions (1) and (2) above have been computationally modelled assuming a direct reaction of ozone with NO_x proceeding via formation of transition states followed by breaking of the $O\text{-}O_2$ bond according to the following schemes:

$$NO + O_3 \rightarrow \{ON\ldots O\ldots O_2\}^{\ddagger} \rightarrow NO_2 + O_2 \quad (5)$$

$$NO_2 + O_3 \rightarrow \{O_2N\ldots O\ldots O_2\}^{\ddagger} \rightarrow NO_3 + O_2 \quad (6)$$

In the present study we applied four different quantum chemical models to characterize the potential energy surface of a system comprising nitrogen oxide reacting with ozone:

HF, MP2, DFT/ B3LYP and CCSD**.** Energy was computed as a function of the distance between the N-atom of the nitrogen oxide and the O-atom of ozone. All calculations were carried out using the Gaussian 03 [3] suite of programs for electronic structure calculations. All calculations were performed using the 6-311g (d, p) basis set.

To compute the potential energy scans, the distance between the N-atom of nitrogen oxides (NO and NO_2) and the O-atom of ozone was systematically varied between 1.25Å and 2.50Å in increments of 0.05Å. At each point, the geometries were optimized using HF, MP2 and B3LYP levels of theory. For calculations using the CCSD quantum chemical method, the structures optimized at MP2 levels of theory were used and only single point calculations were carried out. The optimized geometries were verified as global minima by carrying out the frequency calculations. The geometries with positive frequency values were considered to minima while the geometries with one negative frequency correspond to transition states. The grids were intensified between 1.40Å and 1.80Å to increments of 0.01Å to better locate any transition states.

Following results from these calculations, reactions (1) and (2) were again modeled using the MP2 level of theory but at higher energy scan resolution with varying finer increments down to as low as 0.0001Å and with three different basis sets, namely 6-311G(d,p) , cc-pVDZ and aug-cc-pVDZ.

The plots of potential energy vs. N-O bond distance for the reactions of NO and NO_2 with O_3 indicated the presence of transition states in both reactions in the HF, MP2 and CCSD models but no clear indication could be seen in the B3LYP analysis. N-O bond distance for the O_3-NO reaction was indicated at about 1.6 Å by all three positive models while N-O bond distance for the O_3-NO_2 reaction was calculated at 1.6 Å by the MP2 and CCSD techniques and at 1.78 Å by the HF method.

Table 2. Calculated N-O distance during O_3-NO and O_3-NO_2 reactions.

	O_3-NO Reaction		O_3-NO_2 Reaction	
Model	Transition State Indicated	N-O Distance	Transition State Indicated	N-O Distance
HF	Yes	1.62Å	Yes	1.78Å
MP2	Yes	1.6Å	Yes	1.61Å
B3LYP	No	-	No	-
CCSD	Yes	1.59Å	Yes	1.6Å

A tentative conclusion could be drawn that the reactions of ozone with nitrogen oxides do not go directly from reactants to products but involve at least one intermediate state. Further analysis would require multi-reference wave functions, such as obtained from CASSCF calculations, and inclusion of dynamical correlations energy via second order multi-reference perturbation theory.

In an attempt to better define the potential energy surfaces, the MP2 level of theory was further applied to reactions (1) and (2) with three different basis function sets and finer potential energy scan resolution. Figure 3 shows the potential energy surface for the three basis sets for reaction (1) (NO with O_3) and Figure 4 shows the same for reaction (2) (NO_2 with O_3).

These finer energy scans show the presence of transition states. With respect to reaction (1) of NO with O_3, the MP2/6-311g(d,p) and MP2/cc-pVDZ basis sets show the transition state at an N-O distance of 1.605Å while in the MP2/aug-cc-pVDZ basis set the transition state is at 1.6146Å and, in this case, the transition state is an in-plane type complex as

shown in Figure 1. With respect to reaction (2) of NO_2 with O_3, all three basis sets showed a transition state at an N-O bond distance of 1.626Å in the form of a non-planar complex as shown in Figure 2.

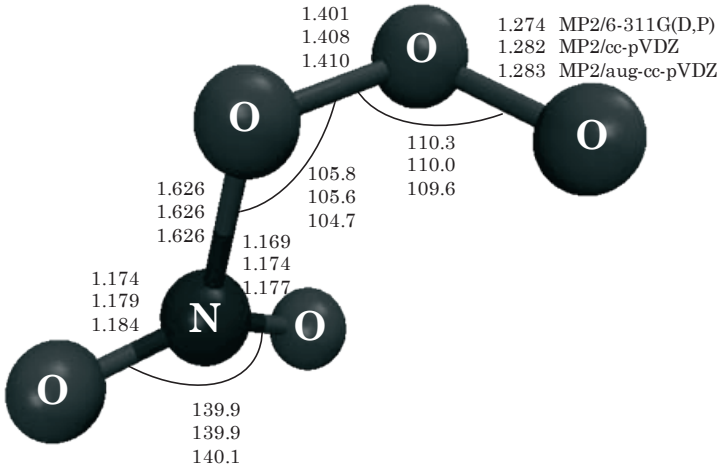

Fig. 1. The molecular and transition state geometrical (NO+ O_3) parameters obtained at the MP2/6 311G(d,p), MP2/cc-pVDZ and MP2/aug-cc-pVDZ levels theory (bond lengths in Å, valence angles in degrees)

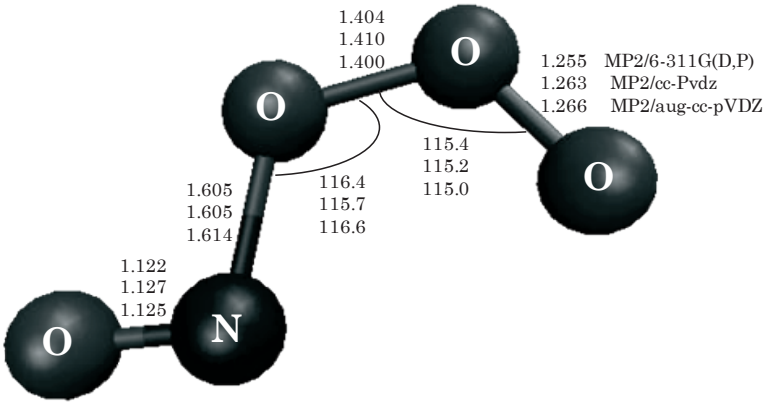

Fig. 2. The molecular and transition state geometrical (NO_2 +O_3) parameters obtained at the MP2/6-311G(d,p), MP2/cc-pVDZ and MP2/aug-cc-pVDZ levels theory (bond lengths in Å, valence angles in degrees)

For reaction (1) NO + O_3, E_a was calculated to be 1.1 kcal/mol for the 6-311G(d,p) basis set, 1.3 kcal/mol for the cc-pVDZ basis set and 2.2 kcal/mol for the aug-cc-pVDZ basis set. This compared reasonably well with the experimental Arrhenius activation energy of 1.2 kcal/mol.

For reaction (2) NO_2 + O_3, E_a was calculated to be 8.7 kcal/mol for the 6-311G(d,p) basis set, 8.5 kcal/mol for the cc-pVDZ basis set and 8.2 kcal/mol for the aug-cc-pVDZ basis set, a factor of 4 higher than the experimental Arrhenius activation energy of 2.2 kcal/mol.

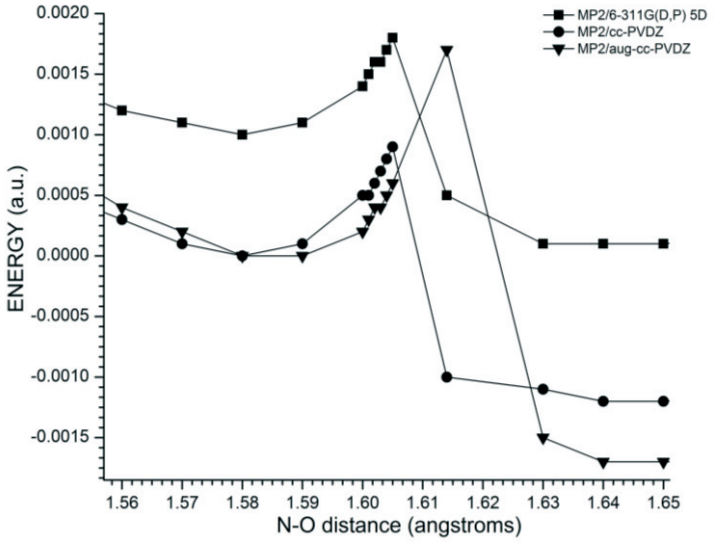

Fig. 3. Potential energy vs. N-O distance for the reaction of O_3 with NO modeled using the MP2 level of theory with three basis sets, 6-311G(d,p), cc-pVDZ and aug-cc-pVDZ

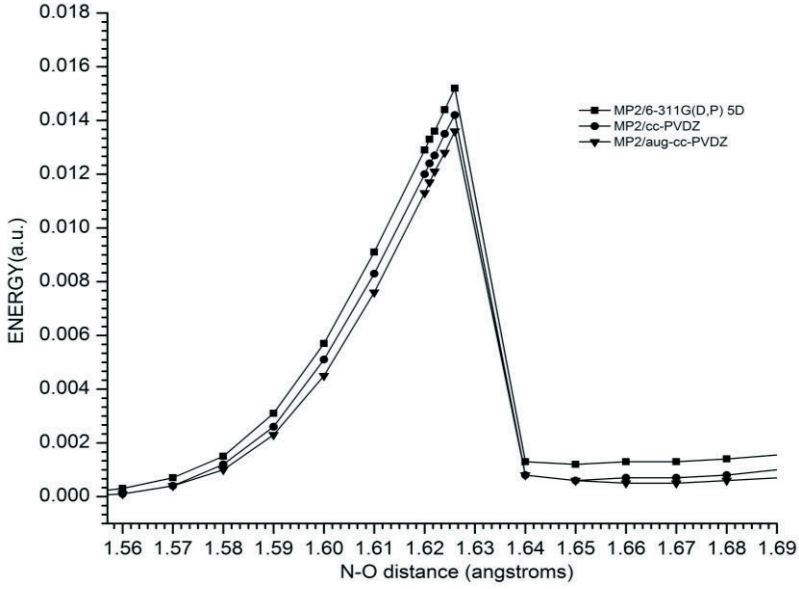

Fig. 4. Potential energy vs. N-O distance for the reaction of O_3 with NO_2 modeled using the MP2 level of theory with three basis sets, 6-311G(d,p), cc-pVDZ and aug-cc-pVDZ

3. Conclusions

The NO_x – O_3 reaction oxidation processes, well known at the molecular level, were modelled by ab initio quantum chemistry methods in an attempt to calculate the total reaction energy, E_t, detect the presence of any transition states and to calculate the activation energy, E_a, of individual reactions.

Application of the DFT quantum chemistry model indicates that all of the reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (7)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (8)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \quad (9)$$

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \quad (10)$$

corrected for zero-point energy are exothermic with reaction energies ranging from -16.90 to – 62.31 kcal/mol.

Application of the HF, MP2 and CCSD quantum chemistry models indicate the presence of intermediate or transition states in the initializing reactions of the overall reaction chain, namely reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (11)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (12)$$

Application of the MP2 quantum chemistry model with three different basis function sets and finer potential energy scan resolution shows the presence of transition states with defined structures and enables calculation of the activation energies, E_a, for chain initializing reactions (1) and (2) above.

Acknowledgements

We acknowledge support from Polish Ministry of Science and Higher Education within the statutory research number S/12/II B/2016.

References

1. PQS version 3.1, Parallel Quantum Solutions, 2013 Green Acres Road, Fayetteville, Arkansas 72703, USA.
2. Helgaker T., Jensen H.J.Aa., Joergensen P., Olsen J., Ruud K., Aagren H., Auer A.A., Bak K.L., Bakken V., Christiansen O., Coriani S., Dahle P., Dalskov E.K., Enevoldsen T., Fernandez B., Haettig C., Hald K., Halkier A., Heiberg H., Hettema H., Jonsson D., Kirpekar S., Kobayashi R., Koch H., Mikkelsen K.V., Norman P., Packer M.J., Pedersen T.B., Ruden T.A., Sanchez A., Saue T., Sauer S.P.A., Schimmelpfennig B., Sylvester-Hvid K.O., Taylor P.R., Vahtras O. *Dalton, a molecular electronic structure program*, Release 1.2, 2001.
3. Frisch J. et al. *Gaussian 03, Revision V.05*, M. Gaussian, Inc., Wallingford, CT, USA , 2004.
4. Jaroszyńska-Wolińska J., Kumar M., *Quantum chemical modeling of the ozone –based NOx oxidation process*. Proceedings of the 11th Annual International Symposium of the HAKONE, Oleron Island, France, 7-12 September 2008, Vol.2, pp. 402-407.
5. Jaroszyńska-Wolińska J., Garabato B. D., Alam J., Reza A., Kozłowski P.M. Structural and electronic properties of an [(Al2O3)4]+ cluster Journal of Molecular Modeling 21 2015 170-179.