Unconventional Channel of Atmospheric Reaction NO + $O_3 \rightarrow NO_2 + O_2$: a Mechanistic Study Using Born-Oppenheimer Molecular Dynamics

Yago S. de Sousa; Ademir J. Camargo; Heibbe C. Oliveira; Valter H. Carvalho

Introduction

Given the importance of the ozone in the stratosphere against harmful radiation, the understanding of the ozone depletion process become mandatory^{1–3}.

There are several compounds involved in the degradation of ozone and specifically in the stratosphere exist a significant amount of NOx compounds4. Knowledge of these mechanisms has been responsible by a relative abundance of experimental and theoretical work^{4–8}. However, the mechanism involving the NO compound still remains unclear since the experiments observe two differents mechanisms (abstracts an end-O- atom and a central-O-atom) by nitric oxide⁷ and just the first possibility has been elucidaded theoretically.



Scheme1. The two mechanism involved in the reaction of $NO + O_3$.

In this paper, inspired by cross section experimental data, we reported the nonconventional mechanism for the abstraction of central-O-atom using Born-Oppenheimer Molecular Dynamics.

Methods

The structures of all reactive components have been built in the GaussView⁵ program and all theoretical calculations were carried out using the program suite. The proposed reaction G09⁹ pathway has been guided by a centralized attack the N atom to ozone to produce effective collisions reagents for the formation of the desired product. We used the Bohr-Oppenheimer Molecular Dynamics (BOMD)¹⁰ approach to simulate the mechanism. A specified temperature of 0.65eV was adopted. The electronic structure was treated with B3LYP/3-21G. The lower level of these calculations is admittedly, but it is compromise, initially, with the description of the process. The system was built with one NO molecule and one O_3 molecule in the vacuum. A reaction coordinate (Δr) was defined as the difference between lengths of the bond that is progressively broken, r, and of one which is concertedly formed, r₁ (see, Figure 1). At $\Delta \gamma < 0$, the condition given by the reagents, such that it, $\Delta \gamma > 0$, it evidences the formation of the product.



Figure 1. Reaction coordinates used to describe the mechanism.

Results and Discussion

During the numerous simulations, there were certain discrepancies with the abstraction of the central oxygen ozone carried by nitric oxide. Working with STQN method (Synchronous Transit-Guided Quasi-Newton)¹¹, in an attempt of found a stationay transition state involved in the process, this procedure has been ineffective.

The BOMD procedure showed trajectories able to describe the interest mechanism. It was observed a binding between the molecule of NO and O_3 . In the Figure 2, it is showed specifics configuration of the trajectories, point out reactants (A panel), transition state (B panel) and products (C and D panels) with temporal scale of the event.



Figure 2. Temporal evolution of the NO + O_3 reaction using BOMD at B3LYP/3-21G level.

A potential energy profile of the reaction is presented in the Figure 3. The stationary points in the potential curve satisfactorily characterized (A - D)configurations. Transition state is well characterized in the B point, however, there is a unconvention profile in the potential curve: flat region. The shape can explain the inefficiency of the STQN method, a gradient method that demands well defined stationary point.



Figure 3. Potential energy profile for the NO + $O_3 \rightarrow NO_2 + O_2$ reaction.

As discussed, the flat region represented by B indicates the noticeable maximum value, which, this point corresponds to the transition state, with 5 kcal. mol⁻¹ barrier height, approximately. The minimum stationary point (A and D) in the potential curve defined the reactants and products, respectively.

Conclusion

In summary, the BOMD procedure was able to describe the unconventional mechanism for the NO + O_3 reaction. The main stationay points were observed in the calculated trajectory. The transition state is localized in the flat region on the potential curve, this result explain the inefficacy of the STQN method. The understanding of this mechanism can be guide the comprehension of the dynamics and kinetics parameters involved in the depletion of the ozone in the stratosphere. In addition,

othres trajectories are being calculated with high level ab initio methods.

Acknowledgments

The authors are grateful for the support given from the FAPEG, CAPES, CNPQ and FINATEC.

References

- 1. Heinhorst, S. & Cannon, G. C. J. Chem. Educ. 86, 150 (2009).
- 2. Read, K. A. et al. Nature 453, 1232-5 (2008).
- Savarino, J., Bhattacharya, S. K., Morin, S., Baroni, M. & Doussin, J.-F. J. Chem. Phys. 128, 194303 (2008).
- Dutta, A. K., Vaval, N. & Pal, S. J. Chem Theory Comput. 8, 1895–1901 (2012).
- Kahler, C. C., Ansell, E., Upshur, C. M. & Green, W. H. J. Chem. Phys. 80, 3644 (1984).
- 6. Kahler, C. C. & Kowalczyk, M. J. Chem. Phys. 84, 1946 (1986).
- 7. Ende, D. van den. J. Chem. Phys. 77, 2206 (1982).
- Jaroszyńska-Wolińska, J. J. Mol. Struct. THEOCHEM 952, 74–83 (2010).
- 9. Frisch, M. J. et al. Gaussian 09 Revision D.01. (2009).
- Marx, D. & Hutter, J. Mod. methods algorithms quantum Chem. 1, 301–449 (2000).
- Peng, C. & Bernhard Schlegel, H. Isr.J. Chem. 33, 449–454 (1993).

Yago S. de Sousa¹; Ademir J.Camargo¹; Heibbe C. Oliveira² & Valter H. Carvalho^{1,*}

^aGrupo de Química Teórica e Estrutural de Anápolis, Campus de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, 75001-970, Anápolis, Brasil

^bInstituto de Química, Universidade de Brasília, 70904-970,Brasília, Brasil.

*fatioleg@gmail.com