Unconventional Channel of Atmospheric Reaction NO + O_3 → NO_2 + O_2: A Mechanistic Study Using Born-Oppenheimer Molecular Dynamics

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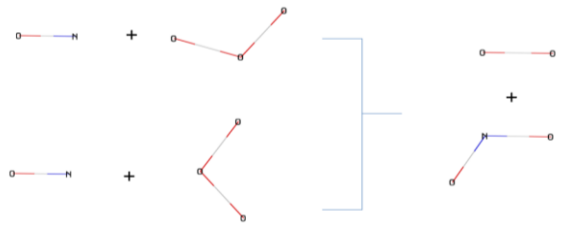
INTRODUCTION

Due to the importance of the ozone in the stratosphere for protection against harmful radiation, understanding the ozone depletion process becomes mandatory[1–3].

There are several compounds involved in the degradation of the ozone, and specifically in the stratosphere there exists a significant amount of NO_x compounds[4]. Knowledge of these mechanisms has been obtained by a relative abundance of experimental and theoretical work[4–8]. However, the mechanism involving the NO compound still remains unclear, since experiments observe two different mechanisms (abstracts with an end-O-atom and a central-O-atom) by nitric oxide[7], and only the first possibility has been elucidated theoretically.



Scheme 1. The two mechanism involved in the reaction of NO + O_3.

In this paper, inspired by cross section experimental data, we reported a non-conventional mechanism for the abstraction of the 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 G09[9] program suite.The proposed reaction pathway was guided by a centralized attack of the N atom in the ozone to produce effective collision 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 the B3LYP/3-21G level of calculation. 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_2, and one of which is concertedly formed, r_1 (see, Figure 1). At $\Delta r < 0$, the condition given by the reagents, such that it, $\Delta r > 0$, evidences the formation of the product.

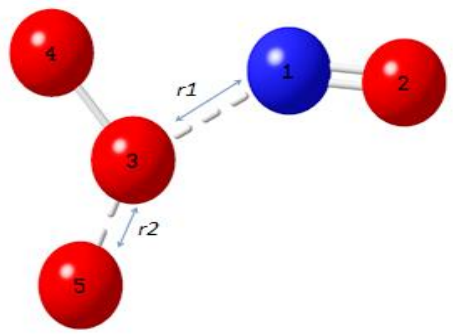


Figure 1. Reaction coordinates used to describe the mechanism.

RESULTS AND DISCUSSION

During numerous simulations, there were certain discrepancies with the abstraction of the central oxygen ozone carried by nitric oxide. Working with the STQN method (Synchronous Transit-Guided Quasi-

Newton)[11], in an attempt to find a stationary transition state involved in the process, this procedure has been ineffective.

BOMD procedure showed trajectories capable of describing the mechanism of interest. A binding between the NO and O_3 molecules was observed.In Figure 2, specific configurations of the trajectories were shown; point out reactants (A panel), transition state (B panel) and products (C and D panels) with temporal scale of the event.

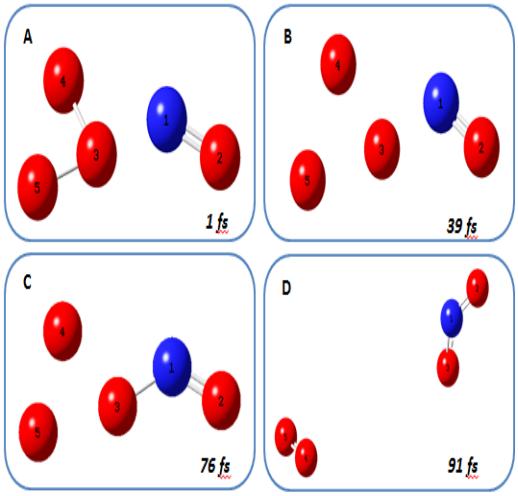


Figure 2. Temporal evolution of the NO + O3 reaction using BOMD at B3LYP/3-21G level.

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

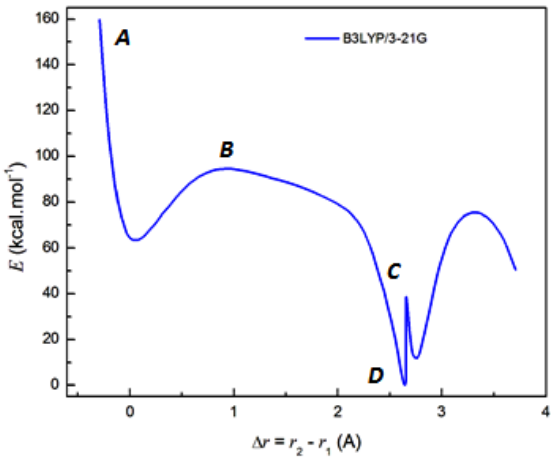


Figure 3. Potential energy profile for the NO + $O_3 \rightarrow NO_2 + O_2$ reaction.

As previously discussed, the flat region represented by B indicates a noticeable maximum value. This point corresponds to the transition state, with an approximately 35 kcal.mol^{-1} barrier height. The minimum stationary points (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 + O3 reaction. The main stationary points were observed in the calculated trajectory. The transition state is localized in the flat region on the potential curve. This result explains the inefficacy of the STQN method. Understanding this mechanism can be a guide for comprehending the dynamics and kinetic parameters involved in the depletion of the ozone in the stratosphere. In addition, other trajectories are being calculated with high level *ab initio* methods.

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