

A Possible Reaction Channel from BrONO to BrNO₂

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Abstract: A possible isomerization channel from BrONO (bromine nitrite) to BrNO₂ (nitryl bromide) is predicted by means of MP2 and QCISD(T) (single-point) methods. The channel is a direct bromine abstraction reaction from BrONO molecule by NO₂ in which the forward reaction barrier is 89.30 kJ/mol at final UQCISD(T)/6-311+G(2df)//UMP2/6-311G(d) level of theory with zero-point energies included. The result can explain the available experiments very well.

Keywords: BrNO₂, BrONO, isomerization, abstraction.

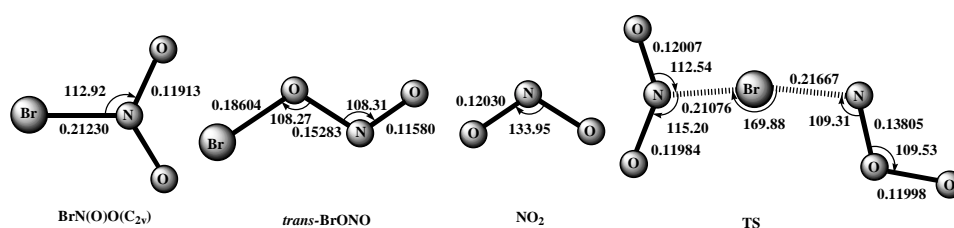
The reaction between bromine atoms and NO₂ has attracted much attention because of the potential importance of BrNO₂ and its isomers in the atmosphere, and many experimental and theoretical studies have been performed on the preparation, spectra, structures, vibrational frequencies, bonding and heats of formation¹⁻⁹. In previous experiments²⁻⁴, BrNO₂ was found to be the major product in the reaction of bromine with NO₂. But very recently, Orlando and his coworker⁵ considered the BrONO, an isomer of BrNO₂, as the major product in similar reaction system. And then, some differences in experimental conditions or assignment of products were expected to exist. Therefore, a detailed knowledge about the isomerization and possible reaction mechanism is very desirable and helpful for interpreting the available experiments.

In several experiments²⁻⁴, BrNO₂ was considered as the major product in the gas phase reaction of Br with NO₂, and in following photolysis experiments *cis*-BrONO and/or *trans*-BrONO were found to appear in the reaction system, which indicated obviously the existence of the isomerizations BrNO₂→*trans*-BrONO→*cis*-BrONO. From computed results we can easily know that the isomerization barrier for BrNO₂→*trans*-BrONO is higher than 210.00 kJ/mol (all energies in the paper were obtained at UQCISD(T)/6-311+G(2df)//UMP2/6-311G(d) with zero-point energies inclusion), and the reverse barrier is about 171.83 kJ/mol. In the view of higher thermodynamical stability of *cis*-BrONO than *trans*-BrONO by 14.24 kJ/mol (this work), we can safely expect *cis*-BrONO and BrNO₂ to be kinetically stable species. Furthermore, our computational results also show that the reaction between Br and NO₂

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will directly lead to the formation of *cis*-BrONO with a 9.76 kJ/mol reaction barrier height. The mechanism is in agreement with Orlando's experiment⁵ in which *cis*-BrONO is the major product. Based on the reaction mechanism, in discussed experiments²⁻⁴ with the major product BrNO₂, the first-step product is also expected to be BrONO followed by the isomerization BrONO→BrNO₂. But the isomerization can not seem to happen because of the 171.83 kJ/mol reaction barrier height. Unfortunately, BrONO are almost turned to BrNO₂ in these experiments²⁻⁴ except Orlando's one⁵. After noting some differences in these experiments, we reasonably think that the concentration of NO₂ plays an important role in the systems. **Figure 1** indicates the optimized geometries of some stationary points in the reaction *trans*-BrONO + NO₂ → TS → BrNO₂ + NO₂ (1). TS is bromine abstract reaction transition state which is approved to accurately connect the reactants and products in (1) by means of intrinsic reaction coordinate calculations at UMP2/6-311G(d) level. The abstract reaction barrier is only 89.30 kJ/mol, which is lower than the direct isomerization barrier 171.83 kJ/mol for *trans*-BrONO → BrNO₂. But process (1) is a bimolecular reaction, and it greatly depends on the concentrations of reactants. In experiments²⁻⁴ with major product BrNO₂, the concentration of NO₂ is in large excess over Br, which makes the reaction (1) happen easily and lead to the formation of product BrNO₂. But in Orlando's experiment⁵, NO₂ is almost equivalent in concentration with Br, which can not make the reaction (1) happen sufficiently, and the final product is BrONO. Therefore, our computational results are in good agreement with the available experiments, and predict a very possible low-barrier reaction pathway from BrONO to BrNO₂ in enriched-NO₂-containing system.

Figure 1 Predicted geometries of stationary points at UMP2/6-311G(d) level of theory. Bond lengths are in nanometers, and bond angles in degrees



Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 20171015, 20171016), the Natural Science Foundation of Heilongjiang Province of China (No. E00-16), and the Science Foundation for Excellent Youth of Heilongjiang University (2002).

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Received 22 February, 2002

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