AB INITIO STUDY OF THE OXIDATION OF NCN BY O_2

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I. Introduction

NCN is the major radical formed in the new prompt NO reaction, CH + N_2 → HNCN → NCN + H.[1] The oxidation of NCN radicals to NO is critical to our full understanding of the prompt NO formation mechanism.

In this series of studies, we have investigated the reactions of NCN with O, OH[2] and O_2 by ab initio MO calculations. We report here the result for the latter process NCN + O_2.

II. Computational Methods

The potential energy surface (PES) was calculated at the highest scheme of the G2M method.[3] The Gaussian 03 program[4] was used for the molecular orbital calculations.

The rate constants were computed with microcanonical variational RRKM (Variflex) code.[5]

III. Results and Discussion

A. Potential Energy Surface and Reaction Mechanism

The optimized geometries of the intermediates and transition states are shown in Figure 1. The potential energy diagram obtained at the G2M(CC1)//B3LYP/6-311G(d, p) level is presented in Fig. 2.

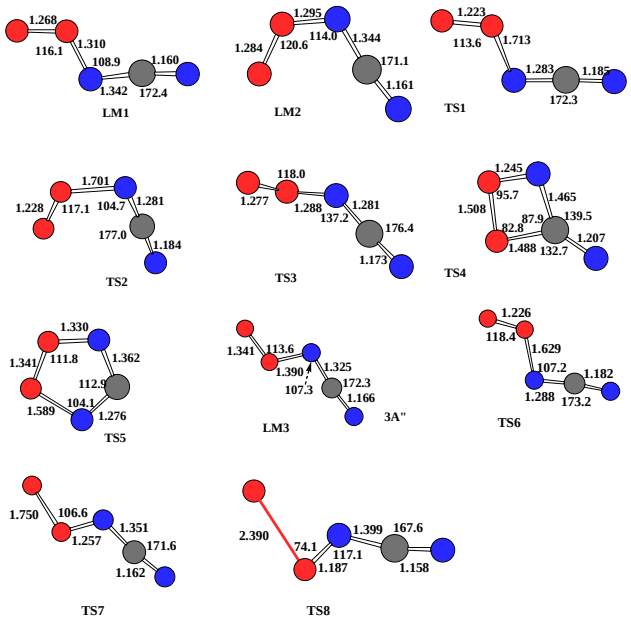

Figure 1. The optimized geometry of intermediates and transition states computed at the B3LYP/6-311G(d, p) level for the NCN + O_2 reaction.

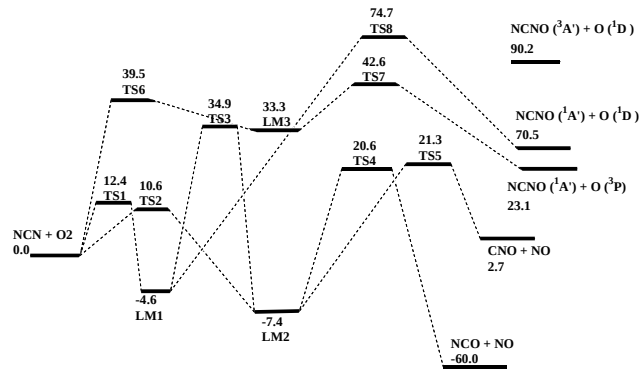

Figure 2. The schematic diagram of the potential energy surface for the NCN-O_2 system computed at the G2M(CC1) level.

The following possible channels are considered for this oxidation reaction:

$$NCN + O_2 \rightarrow NCNOO^{\dagger} \rightarrow NCO + NO \quad (1)$$
$$\rightarrow CNO + NO \quad (2)$$
$$\rightarrow NCNO + {}^{1,3}O \quad (3)$$

The lowest energy isomer is cis-trans-OONCN (LM2), it lies below the reactants by 7.4 kcal/mol at the G2M(CC1) level. It can dissociate to NCO + NO and CNO + NO via four- and five-member ring transition states with barriers of 28.0 and 28.7 kcal/mol. The entrance barrier for this channel is 10.6 kcal/mol. The other isomer, trans-trans-OONCN intermediate (LM1) lies below the reactants by 4.6 kcal/mol with a entrance barrier of 12.4 kcal/mol, which dissociates to NCNO + ^{1}O via a transition state with high barrier, 79.3 kcal/mol. In addition, the stability of the triplet intermediate is also considered, the results show that ^{3}A" trans-trans-OONCN (LM3) lies above the reactants by 33.3 kcal/mol, which means that the triplet path is not favorable for this reaction.

B. Rate constant calculations

The rate constants are calculated in the temperature range of 1000 - 3000 K, the results show that oxidation NCN by O_2 to produce NCO + NO and CNO + NO is rather slow because of the high entrance and exit barriers. The total rate can expressed as:
$k_t = 7.29 \times 10^{-15}\ T^{0.51} \exp(-12365/T)$ cm^3 molecule^{-1} s^{-1}.

IV. Conclusion

The mechanism for the oxidation of NCN by O_2 has been discussed and rate constants for the low-lying channels are calculated. The results show that oxidation NCN by O_2 to produce NCO + NO and CNO + NO is very slow because of the high entrance and exit barriers. This reaction can not compete effectively with the much faster oxidation processes, NCN + O and OH.[2]

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