A Kinetics and mechanistic study of two 1,3-dipolar cycloaddition reactions type

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INTRODUCTION & AIM

It is well-known that the reaction of 1,3-dipolar cycloaddition (1,3-DC) is a powerful and very useful synthetic approach for the formation of a variety of heterocyclic compounds found in many crucial and important areas of study and research such as; biology, chemistry, botanic, agronomy, etc. Nitrones, among many other reactants, are only some of the usual 1,3-dipoles employed to build such heterocycles in presence of dipolarophiles as olefines or also known as alkenes. The combination of these latter in a given cycloaddition reaction conducts to the construction of isoxazolidines, N,O-heterocycles. This type of reaction has gained its fame because of the highly selectivity it gives which makes of it one of the target reactions in the world of organic chemistry synthesis. They are both step-economical and environmentally friendly.

In this study, the most popular density functional theory (DFT) B3LYP method has been used to characterize two 1,3-dipolar cycloaddition.

METHOD

The calculations of the reaction under study have been done at B3LYP/6-31G(d) using Gaussian 09 and GaussView suit of programs. Parr functions have calculated using the atomic spin density of Mulliken (ASD). Local electrophilicity and nucleophilicity have been calculated using the polar model of Domingo et al.

RESULTS & DISCUSSION

Table 1 : Parr functions, local electrophilicity and nucleophilicity for nitrone 5 at B3LYP/6-31G(d).

Atom k	P^+	P^-	ω_k^+	N_k
C1	0.00	0.00	0.00	0.01
C2	-0.04	-0.01	-0.03	-0.02
C3	-0.04	-0.02	-0.03	-0.09
N10	0.36	-0.07	0.27	-0.24
O11	0.15	0.66	0.11	2.46
C12	0.48	0.38	0.36	1.42

Table 2 : Parr functions, local electrophilicity and nucleophilicity for nitrone 6 at B3LYP/6-31G(d).

| Atom k	P^+	P^-	ω_k^+	N_k
O1	0.12	0.70	0.17	2.77
N2	0.34	-0.04	0.47	-0.18
C3	0.00	0.00	0.00	-0.01
C6	0.00	0.00	0.00	0.01
C9	-0.04	-0.02	-0.06	-0.06
C12	-0.04	-0.01	-0.06	-0.02
C15	0.49	0.32	0.66	1.28

Table 3 : Parr functions, local electrophilicity and nucleophilicity for *trans*-but-2-ene at B3LYP/6-31G(d).

Atom k	P^+	P^-	ω_k^+	N_k
C1	0.49	0.44	0.24	1.32
C3	0.49	0.44	0.24	1.32
C5	-0.04	-0.01	-0.02	-0.03
C9	-0.04	-0.01	-0.02	-0.03

RESULTS & DISCUSSION
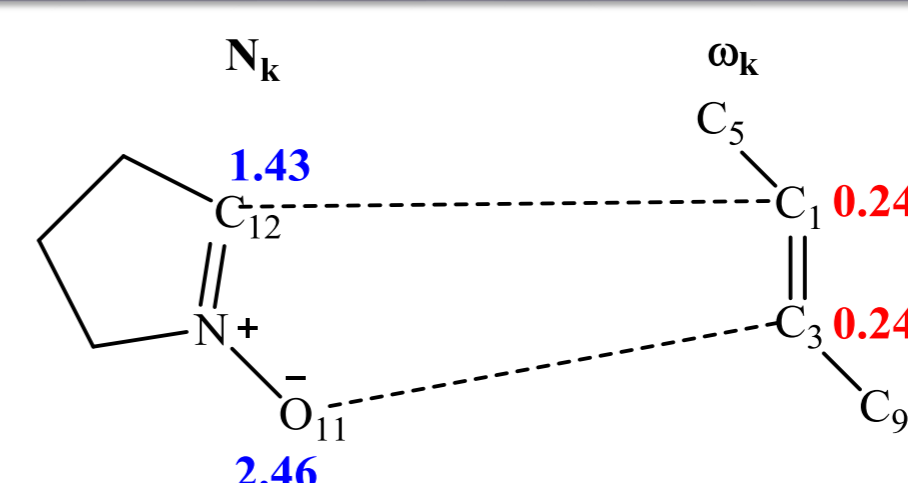
Scheme 1: Reaction with nitrone 5 at B3LYP/6-31G(d).
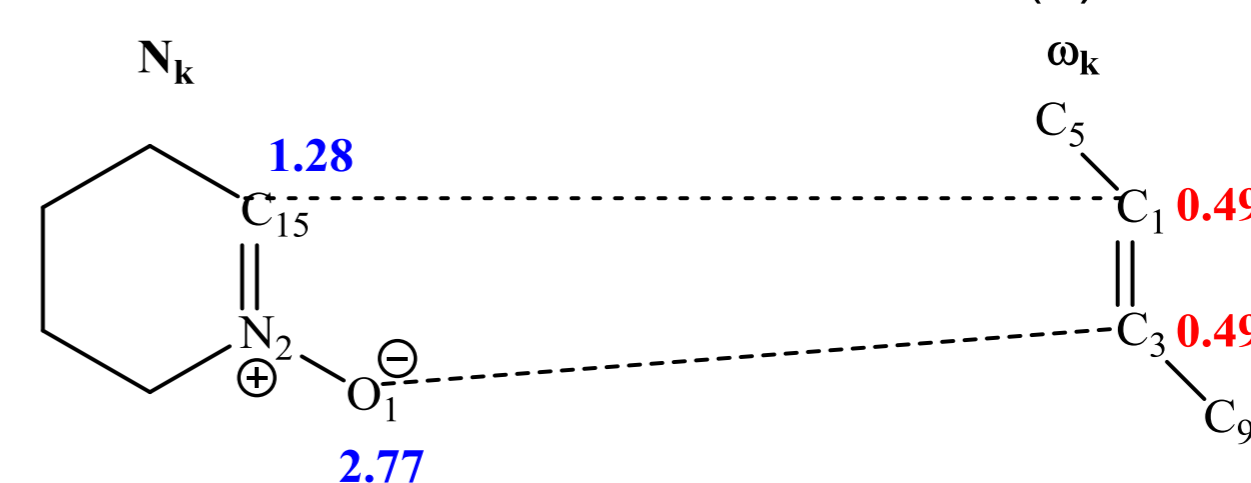
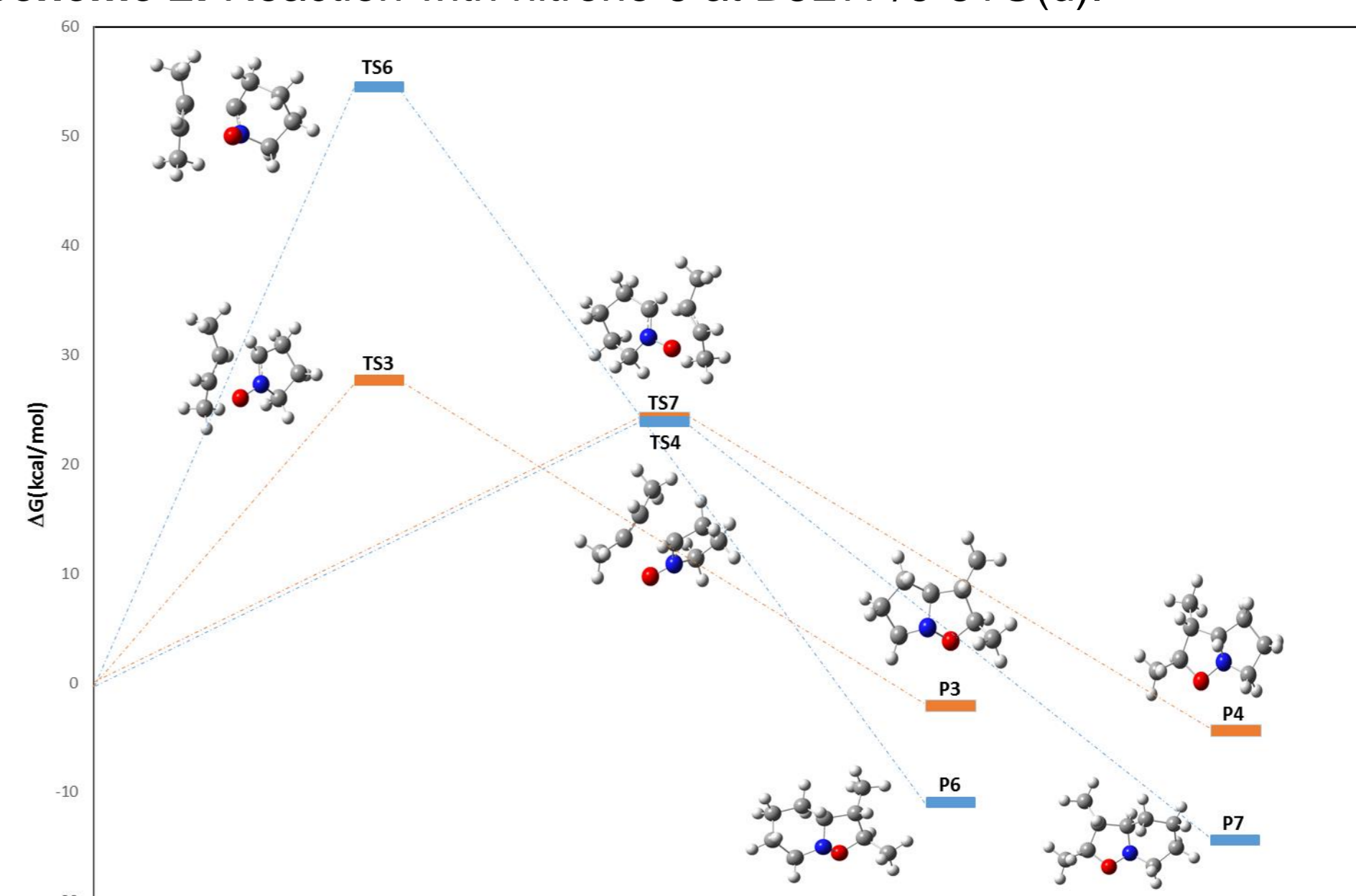**Scheme 2:** Reaction with nitrone 6 at B3LYP/6-31G(d).

Figure 1: Energetic profile of the studied reactions at B3LYP/6-31G(d).

CONCLUSION

The theoretical study has been done at B3LYP method in conjunction with 6-31G(d) basis set.
- The electrophilicity and nucleophilicity calculations show that nitrone 5 and 6 are the nucleophiles while the studied alkenes is the electrophile.
- Parr functions reveals that the most nucleophilic sites of both nitrones are the carbon and oxygen atoms. However, carbon atoms of the double bond of the trans-but-2-ene are the most electrophilic sites.
- The obtained products of nitrone 6 are more favored kinetically and thermodynamically under a concerted mechanism.

FUTURE WORK / REFERENCES

1. Abu-Orabi, S. T., Atfah, M. A., Jibril, I., Mari'i, F. M., & Ali, A. A. S. (1989). Dipolar cycloaddition reactions of organic azides with some acetylenic compounds. *Journal of heterocyclic chemistry*, 26(5), 1461-1468.
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3. Abbiche, K., Mohammad-Salim, H., Salah, M., Mazoir, N., Zeroual, A., El Alaoui El Abdallaoui, H., ... & Hochlaf, M. (2020). Insights into the mechanism and regiochemistry of the 1, 3-dipolar cycloaddition reaction between benzaldehyde and diazomethane. *Theoretical Chemistry Accounts, 139*, 1-12.