

Regioselectivity in Chemical Reactions, Using Shannon Information Entropy

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Introduction

Diels-Alder reactions have a special importance in organic chemistry.[1] When both of the reagents in this reaction are asymmetrically substituted, regioselectivity is observed [2]. The Paterno-Büchi reaction, the formation of oxetanes via photochemical [2+2] cycloaddition of carbonyl compounds to alkenes, is the most general method for the synthesis of four-membered oxygen heterocyclic rings in a regioselective manner.[3,4]

Information theory is a branch of mathematics introduced by Shannon. The concept of Shannon entropy is the central role of information theory sometimes referred as measure of uncertainty. The Shannon entropy $S(r)$ of electron density $\rho(r)$ in the position space is defined as:[5]

$$S(r) = - \int \rho(r) \ln \rho(r) dr \quad (1)$$

In this study it is attempted to investigate the regioselectivity of the mentioned reactions using one of the the information theory concepts; Shannon entropy.

Computational methods:

A B3LYP/6-31G** method is adopted within the Gaussian 98W programs, to optimize all calculations. To compute the corresponding parameters, we need to perform geometry optimization on the neutral molecules (N-electron system), and then single point calculations on the cation ($N - 1$) and anion ($N + 1$) forms of the molecule at the neutral geometry. The Shannon information entropy values were also calculated for each reaction site using the Multiwfn 2.5.2.

If shape function is used ($\frac{\rho(r)}{N}$), the normalized Shannon entropy is given by:

$$S(r) = - \int \frac{\rho(r)}{N} \ln \frac{\rho(r)}{N} dr \quad (2)$$

And the following parameters are used for study the regioselectivity of a given species:

$$\zeta^+(\mathbf{r}) = S_{N+1}(\mathbf{r}) - S_N(\mathbf{r}) \text{ for the nucleophilic attack} \quad (3a)$$

$$\zeta^-(\mathbf{r}) = S_N(\mathbf{r}) - S_{N-1}(\mathbf{r}) \text{ for the electrophilic attack} \quad (3b)$$

$$\zeta^0(\mathbf{r}) = 1/2 [S_{N+1}(\mathbf{r}) - S_{N-1}(\mathbf{r})] \text{ for the radicalar attack} \quad (3c)$$

When atoms i and j of molecule A are involved in the formation of a cycloadduct with atoms k and l of molecule B, the following quantity is defined [6]:

$$\Delta_{ij}^{kl} = (\zeta_i - \zeta_k)^2 + (\zeta_j - \zeta_l)^2$$

Results and discussion:

In Diels–Alder reactions (Fig. 1) for a 1-substituted diene, ortho or meta cycloaddition is possible (ortho isomer is preferred). Reaction with a 2-substituted diene yields para and meta cycloadducts (para isomer is favoured) [3]. We first classify the reactants as electrophilic and nucleophilic and then calculated $\zeta^+(r)$, $\zeta^-(r)$ for reaction sites and Δ_{24}^{13} , Δ_{23}^{14} for possible additions [3]. It is shown that the proposed concept can correctly predict the active sites in both kinds of Diels–Alder reactions and in all cases Δ_{24}^{13} is minimum for the preferred reaction. The same procedure is applied for a series of Paternò–Büchi reactions (Fig. 2) [4,5]; and again in all cases the introduced concepts successfully predicts the major products of reactions. For these reactions calculated $\zeta^0(r)$ for reaction sites and Δ_{24}^{13} , Δ_{23}^{14} .

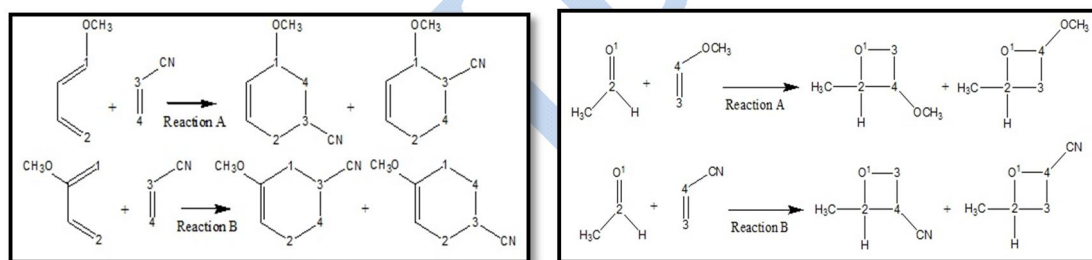


Fig 1. An example of Diels–Alder reactions in this study. **Fig 2.** An example of Paternò–Büchi reactions in this study.

Conclusions

The regioselectivity for a numerous Diels–Alder and Paternò–Büchi reactions has been studied within a density functional framework based on the local Shannon entropy concept in information theory. In the considered reactions, Shannon information entropy successfully predicts the major products with lower Δ .

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