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Computational modelling of the kinetics and thermodynamics of Diels-Alder reaction: 1, 3-cyclohexadiene and substituted ethene

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Abstract

The kinetics and thermodynamics of the Diels-Alder reaction of 1-3, Cyclohexadiene and substituted ethene were modelled in the using Density Functional Theory (DFT) at B3LYP level with 6-311++G (2df, 2P) basis set. Electron withdrawing and electron donating group were substituted for hydrogen in ethene (dienophile). Geometric, kinetics, thermodynamic parameters and the HOMO/LUMO energy gap were calculated. The values obtained for the change in the bond length (Δd) in the transition state and the reactants showed that the reaction is asynchronous and energy of formation obtained confirms the exothermicity of the reaction using Hammond's postulate. The result obtained showed that that electron withdrawing group (NO_2-substituted dienophile) lowers the activation parameters ΔH*(89.744 kJ/mol); Ea (92.22 kJ/mol); ΔG*(93.916 kJ/mol) and thereby increasing the rate of the reaction as observed with lower rate constant, k value (2.17 x 10^{-2} $mol^{-1}l$ t^{-1}) compared with unsubstituted and OH-substituted dienophile(ΔH*109.794,121.768 kJ/mol) Ea (112.273, 124.247 kJ/mol) and ΔG*(115.158, 128.324 kJ/mol) respectively. The Rho (ρ) value calculated to describe the sensitivity of the reactions to substituent effect for OH (-1.777) showed that the reaction is creating a positive charge and for NO_2 (+0.223eV) is an indication that the negative charge is building up for the stabilization

effect of the reactions. EWG, NO_2 results into the decrease of HOMO-LUMO energy gap and this causes an increase in the feasibility of the reaction, it is observed that NO_2 with energy gap (-2.91eV) are energetically feasible than the OH substituted dienophile and more than the simple Diels-Alder reaction.

Keywords

Diels Alder reaction; Gas-phase; Substituted ethene

Introduction

Diels-Alder reaction (Figure 1) is a [4+2] cycloaddition reaction which involves a molecule with a conjugated π-system (a diene) and another with at least a π-bond (a dienophile) [1]. Diels Alder reactions are important organic reactions and are extensively used in carbon-carbon bond formation in organic reactions [1-7]. Synthetically, the Diels Alder reactions are important cycloaddition reaction and the most important pericyclic reactions. The study of Diels-Alder reaction has attracted interest [2] because of its importance in diene synthesis and a powerful tool in the synthesis of new organic compounds through a six-membered cyclic system [7-13]. Experimental analysis and theoretical calculations showed that the reactions occur through a concerted mechanism, although some occurs in steps [3, 4, 5].

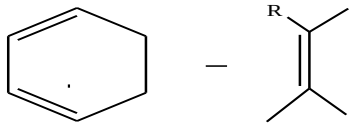


Figure 1. Simple Diels-Alder reaction

The study on prototypical Diels-Alder reactions by hybrid density functional/Hartree-Fock approach showed that the kinetics and the thermodynamic parameters obtained at the B3LYP and QCIST[T] levels approach the experimental value whereas HF and MP2 approaches are not sufficiently reliable [4]. In recent work, substituent effects on simple Diels-Alder reaction as evidence for possible explosive reactions showed that the nature of substituent influences the feasibility of reactions and it also showed the pathway of certain normal and explosive Diels-Alder reactions [6]. Following the work that has been carried out

on kinetics and thermodynamics of Diels-Alder reaction there is dearth of information on the influence of substituent attached to the dienophile on the kinetics and thermodynamic parameters.

Therefore, the aim of this work is to use computational modelling using Spartan calculation model with Density Functional Method at B3LYP level using 6-31G* basis set to study the influence of electron withdrawing group and electron donating groups attached to the dienophile on the kinetic and thermodynamic parameters to show the influence on activation parameters.

Materials and method

Computational methodology

Using Spartan 10 density functional method (DFT) with B3LYP/6-31G* basis set, quantum mechanical calculations were carried out on the reaction using the following systematic and consistent computational procedures:

- Conformational search (MMFF)
- ↓
- Reaction path calculation
- ↓
- Location of the transition state
- ↓
- Characterizing the transition state
- ↓
- Geometric Optimization
- ↓
- Calculations

Conformational search was done on the reactants using molecular mechanics force field (MMFF) to obtain the reactants that has the lowest energy which is indicates the stability of the reactants. Reaction path calculations were carried out using C_5-C_{18} and C_2 -C_{15} as the reaction coordinate this was done by slowly altering the bond distance between C_5-C_{18} and C_2 -C_{15} (5.643Å) to the normal (1.546Å) bond length in the product form in 20 iterations. This was done to obtain the mechanism of the reaction. Optimization was performed on the transition state structure to obtain the true transition state; this was subjected to tests to verify that the transition state structure has only one imaginary vibrational frequency (IR value) and that the saddle point connects the ground state, transition state and product together. The intrinsic reaction coordinates method was also used by optimizing the molecule subject to a

fixed position along the reaction coordinate [7]. Full geometry optimization was then carried out on the structure of the reactants, the transition states and products to obtain the geometric parameters such as bond lengths, bond angles, dihedrals and atomic charges.

Kinetics and thermodynamic calculations was done to obtain the kinetic and thermodynamic parameters. To arrive at a closer approximation of the true energy of the molecules, the sum of the ground state energy and the statistically mechanically calculated data was used Eq. [1], [8].

$$H_i = GSE_i + H_i^{\text{sm}} \quad (1)$$

Where: sm - is the statistically mechanically calculated enthalpy, H- the enthalpy of the specie and GSE- ground state energy.

Substitute this into the initial definition of the heat of reaction we have Eq. [2]:

$$\Delta H_{Rxn} = \left(GSE_{product} + H_{product}^{sm}\right) - \left(GSE_{reactants} + H_{reactants}^{sm}\right) \quad (2)$$

Where: ΔH_{rxn} - change in enthalpy of reaction; GSE - ground state energy of reactants and products and H^{sm} - statistically mechanically calculated enthalpy of reactants and products.

Activation energy (E_a) was calculated Eq. [3]:

$$E_a = \Delta H + RT \quad (3)$$

Where: E_a - activation energy, ΔH - change in enthalpy, R - gas constant and T – temperature.

The entropy of the reaction was calculated by taking the difference of product and reactant entropies that is Eq. [4]:

$$\Delta S_{reaction} = S_{product} - S_{reactants} \quad (4)$$

Where: S - entropy and ΔS - change in entropy.

The Gibbs free energy of activation was calculated using the modified version of the heat of reaction equation. Knowing that Eq. [5].

$$G = H - TS \text{ and } \Delta G^* = \Delta H^* - T\Delta S \quad (5)$$

Coefficient *k* was calculated using Eq. [6]:

$$k(T) = \frac{k_B' T}{h} \exp\left|\frac{-E_a}{RT}\right| \quad (6)$$

Where: k' - the Boltzmann; h - Planck's constants.

Energy of HOMO and LUMO was obtained and the band gap was calculated using Eq. [7]:

$$\text{Band Gap} = E\ HOMO - E\ LUMO \quad (7)$$

Hammonds postulate was used to explain the exothermicity of the reaction and Rho (ρ) value was calculated to describe the sensitivity of the reaction to substituent using Eq. [8]:

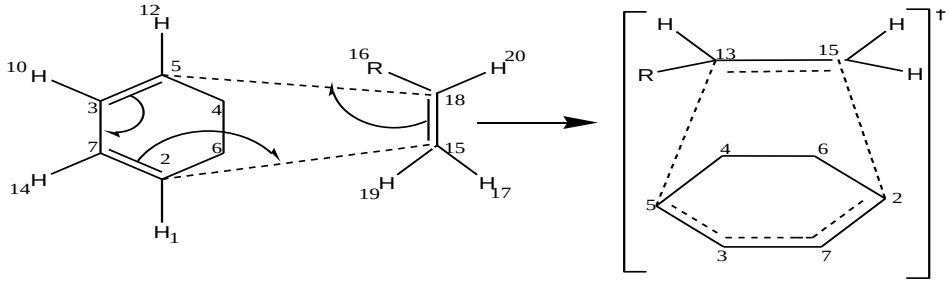
$$\log\left(\frac{K_H}{K_X}\right) = \rho\,\sigma^x \qquad (8)$$

Where: K_H - the equilibrium constant for Hydrogen; K_X - the equilibrium constant for substituent.

Results and Discussion

Reaction mechanism

The reaction proceeds by the normal electron demand through a concerted six-membered cyclic transition state which involves the transfer of electron (breaking of bonds) from three different π-bonds (C_3= C_5, C_2= C_7 and C_{15}= C_{18}) and the formation of one new π-bond between C_3 – C_7 and two new σ-bonds between C_2 – C_{15} and C_5 – C_{18} (Figure 2).



1,3 cyclohexadiene ethene

Figure 2. The reaction mechanism of Diels-Alder reaction of 1,3-cyclohexadiene and substituted ethene

Geometry optimization

Geometry optimization (Figure 3) was done on the reactants, the transition states and the products to obtain the geometric parameters such as bond length, bond angle, dihedral angles and atomic charge distribution (Table 1).

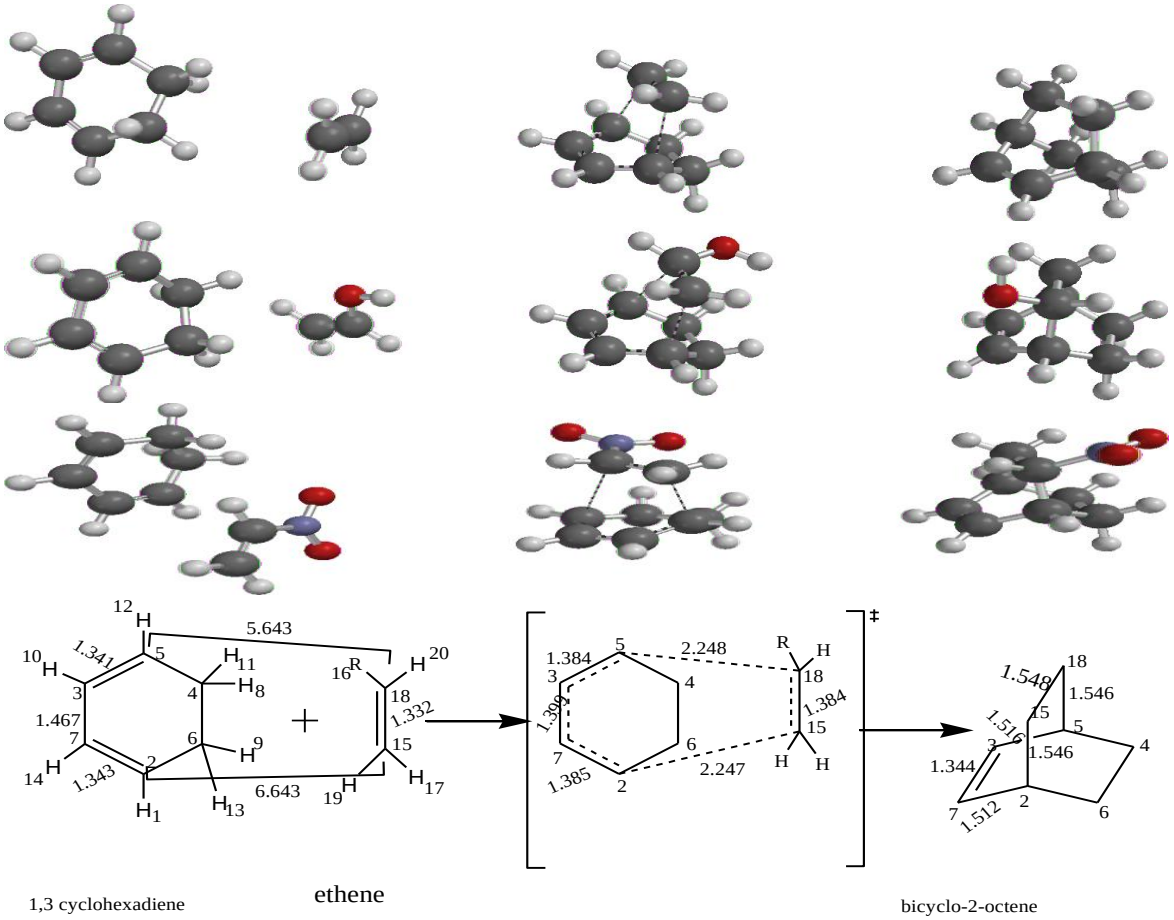


Figure 3. Optimized geometry of the unsubstituted, OH-substituted and NO_2- substituted reactants, transition state and product

Figure 3 shows the optimized geometry of the unsubstituted, OH-substituted and NO_2-substituted structures of ethane in the reactant, transition and product state to explain the process of bond breaking and bond formation of the reaction between 1,3 cyclohexadiene and ethane to form bicyclo-2-octene. The bond length (Figure 3) is the distance between two atoms. Table 1 shows the bond length value for the reactants, transition state and products respectively. Considering the bond distance for (hydrogen) C_3-C_5 (1.341, 1.384 and 1.516Å), the values showed that the ground state reflects the value for a carbon-carbon double bond which increased in the transition state with a sharp increase in the value for the product showing the full assumption of a carbon-carbon single bond. In C_3-C_7 a carbon-carbon single bond exists in the ground state (1.467, 1.399 and 1.344Å) but in the product form a fully formed new pi (π) carbon-carbon double bond emerged. The values obtained in C_2-C_7 and C_{15}-C_{18} (1.323, 1.385 and 1.512; 1.332, 1.384 and 1.548 Å respectively) also showed the disappearance of the double bond for the emergence of the carbon-carbon single bonds in the

product state. Interestingly, at the ground state, no bond exist between C_2 -C_{15} and C_5 and C_{18}, the distances are 6.643 and 5.643 Å but in the transition state it is observed that new bonds are about emerge (2.247 and 2.248 Å) and finally the bond length in the product shows the formation of new carbon-carbon sigma (σ) bonds.

Table 1. Bond length (Å)

Bond Length	States	H	OH	NO_2
$C_3 – C_5$	GS	1.341	1.388	1.338
	TS	1.384	1.381	1.373
	PRD	1.516	1.507	1.509
	Δd	+0.043	+0.043	+0.035
$C_3– C_7$	GS	1.467	1.463	1.464
	TS	1.399	1.396	1.400
	PRD	1.344	1.332	1.337
	Δd	-0.068	-0.087	-0.064
$C_7 – C_2$	GS	1.343	1.337	1.337
	TS	1.385	1.399	1.397
	PRD	1.516	1.508	1.511
	Δd	+0.042	+0.062	+0.060
$C_2 – H_1$	GS	1.088	1.083	1.083
	TS	1.083	1.085	1.084
	PRD	1.094	1.089	1.088
	Δd	-0.005	+0.002	+0.001
$C_5 – H_{12}$	GS	1.088	1.083	1.083
	TS	1.084	1.084	1.085
	PRD	1.094	1.089	1.089
	Δd	-0.004	+0.001	+0.002
$C_{15} – C_{18}$	GS	1.332	1.325	1.319
	TS	1.384	1.394	1.393
	PRD	1.548	1.549	1.537
	Δd	+0.052	+0.069	+0.074
$C_2 – C_{15}$	GS	5.643	5.851	4.611
	TS	2.247	2.435	2.012
	PRD	1.546	1.551	1.556
	Δd	-3.396	-3.416	-2.599
$C_5 – C_{18}$	GS	5.643	5.194	4.793
	TS	2.248	2.066	2.642
	PRD	1.546	1.543	1.549
	Δd	-3.395	-3.484	-1.637

The bold angle (Table 2) shows the interaction between three atoms to determine the specific arrangement of atoms to explain the stability of the molecule. Variation in the values for the reactants, transition and product states is as a result of the distortion that occurs during transition from reactants through the transition state to the products.

Table 2. Bond angle

Bond angle	States	H	OH	NO_2
H_{12} - C_5 - C_3	GS	120.69	120.65	120.60
	TS	119.12	119.57	119.66
	PRD	112.14	112.28	112.36
C_5 - C_3 - C_7	GS	120.64	120.65	119.20
	TS	118.33	120.71	114.33
	PRD	114.39	119.12	114.38
H_{10} - C_3 - C_7	GS	118.71	118.76	118.68
	TS	119.77	119.82	119.73
	PRD	123.82	123.89	123.74
C_7 - C_2 - H_I	GS	120.69	120.65	120.69
	TS	118.96	117.87	117.37
	PRD	112.15	112.67	117.56
C_2 - C_6 - C_4	GS	120.33	120.21	120.20
	TS	112.57	112.36	112.98
	PRD	109.49	109.49	109.29
C_6 - C_4 - C_5	GS	111.72	111.78	112.53
	TS	112.46	112.12	112.98
	PRD	109.24	109.10	109.29
C_{18} - C_{15} - H_{17}	GS	121.77	121.71	120.97
	TS	120.04	122.62	116.30
	PRD	110.87	110.88	109.58
H_{16} -C_{18}-H_{20}	GS	116.44	115.63	111.91
	TS	114.98	111.13	111.99
	PRD	106.48	108.76	102.62

The dihedral angle (Table 3) show the interaction between four atoms and also further explains the stability of the structures. The variation in the values for the ground state, transition state and products are also as a result of the distortion that occurs during the transformation from the reactants to the products.

Table 3. Dihedral angles

Dihedral angles	States	H	OH	NO_2
H_{12} - C_5 - C_3 - H_{10}	GS	-0.88	-0.90	0.09
	TS	-6.07	-1.95	1.67
C_5 - C_3 - C_7 - C_{12}	GS	14.71	14.58	-13.81
	TS	1.03	5.48	5.04
C_6 -C_4 -C_5 -H_{12}	GS	153.21	153.46	-154.21
	TS	170.88	170.54	169.45
C_2 -C_6 -C_4 -C_5	GS	43.09	42.84	-41.06
	TS	3.85	-2.72	-6.87
C_{15} -C_{18} -H_{16} -H_{20}	GS	179.92	-178.82	-179.48
	TS	154.61	3.34	-165.04

C_{18} -C_{15} -H_{17} -H_{19}	GS TS	-179.92 -155.23	179.86 -141.66	-179.91 140.93

The negative values obtained for the enthalpy of reaction (Table 4) ΔH (-111.904, -94.454, and 11.094 for H, OH (electron donating group) and NO_2, electron withdrawing group) respectively showed that the reactions are exothermic.

Negative Gibb's free energy values, ΔG (-99.390, -109.531 and -100.664) showed that the reactions are spontaneous [12]. The activation parameters ΔH* (109.794, 121.768 and 89.744 kJ/mol); E_a (112.273, 124.247 and 92.22 kJ/mol); ΔG* (115.158, 128.324 and 93.916 kJ/mol) for H, OH and NO_2 as reported [13] showed that electron withdrawing group on dienophiles lowers the activation parameters thereby increasing the rate of the reaction as observed with lower rate constant, k value (2.17×10^{-2}) for dienophile substituted with electron withdrawing group NO_2 compared with dienophile substituted electron donating group. The Rho (ρ) calculated (OH -1.777) showed the reaction is creating a positive charge and for NO_2 (+0.223) is an indication that the negative charge is building up for the stabilization effect of the reactions [12].

Table 4. Kinetic and thermodynamic parameters

Parameters	H	OH (EDG)	NO_2 (EWG)
$\Delta H_{reaction}$	-111.906	-94.454	-111.094
$\Delta S_{reaction}$	-42.299	-40.108	-26.042
$\Delta G_{reaction}$	-99.39	-109.53	-100.664
ΔS*	-17.971	-21.289	-13.407
ΔH*	-109.794	-121.768	89.744
Ea	112.273	124.247	92.222
ΔG*	115.158	128.324	93.916
logA	13.731	13.905	13.490
K	1.156×10^{-6}	1.3×10^{-7}	2.17×10^{-2}
K_{eq}	2.581×10^{17}	1.545×10^{19}	4.13×10^{17}
Rho (ρ)	-	-1.777	+0.223

Frontier molecular orbital theory (FMO)

The concertedness and the effect of substituent can be rationalized using FMO. Applying this to this reaction, two modes of interactions are possible, the reaction can be controlled by the interaction of the HOMO of the diene (1, 3-cylohexadiene) with the LUMO of the dienophile (ethene) (the normal electron demand) or by the interaction between the LUMO of the diene and the HOMO of the dienophile (inverse electron demand).

In the former case, a reduction of the diene-HOMO and dienophile-LUMO energy gap (Table 5) can be achieved by raising the energy of the HOMO of the 1,3-cyclohexadiene.

In this reaction, the energy of HOMO (-5.96 eV) is lower compared with the energy of the LUMO (-0.29, -0.49 and -3.06) for the H, OH and NO_2 and this may be as a result of the inverse electron demand.

Table 5. HOMO/LUMO Energy gap

Elements	HOMO (Diene)	LUMO (Dienophile)	Energy gap
H	-5.97	-0.29	-5.68
OH	-5.97	-0.49	-5.48
NO_2	-5.97	-3.06	-2.91

In NO_2-substituted dienophile, the energy gap is far greater than that of OH substituted dienophile and greater compared with simple Diels Alder reactions. This is in line with result obtained by [13]. EWG, as reported [13] results into the decrease of HOMO-LUMO energy gap and this causes an increase in the feasibility of the reaction, notably with NO_2. In this work it is observed that NO_2 with energy gap (-2.91) are energetically feasible than the OH substituted dienophile and more than the simple Diels-Alder reaction.

To determine the concernedness and asynchronicity of the reaction, the electron in the HOMO of 1,3-cyclohexadiene (diene) is like the outer shell electrons of an atom which can be remove with little energy than any of the other electrons in the molecule.

To rationalize the asynchronicity of the reaction [14] bond breaking as shown in the variation of the change in the bond length in the transition state and the reactants (C_3-C_5 Δd = +0.043, +0.043 +0.035; and C_7-C_2 Δd=+0.042, +0.062, +0.060 for H, OH, NO_2 respectively) occur first bond making while the (C_3-C_7 Δd= -0.068, -0.067, -0.064; C_2 -C_{15} Δd=-3.396, -3.416, -2.599 and C_5-C_{18} Δd= -3.395, -3.848, -1.637 for H, OH and NO_2 respectively) is lagging behind.

The energy of formation (Table 7) showed the exothermicity of the reactions was as explained using Hammond's postulate which states that in exothermic steps it is expected that the activation complex resembles the adjacent reactants that it is closest in energy to, as shown in the value of the energy of formation of the transition state for the Diel-Alder reaction between 1,3-cyclohexadiene and substituted, unsubstituted ethene is much more closer to that of the reactants than it is to the products. This is as a result of the formation of the two new σ - bonds.

Table 7. Energy of formation (kJ/mol)

Elements	GS	TS	PRD
H	-819312.375	-819194.25	-819409.50
OH	-1016854.125	-1016715.0	-1016930.25
NO_2	-1356329.625	-1356235.125	-1356429.375

Conclusion

Density Functional Theory (DFT) at B3LYP level with 6-311++G (2df, 2P) basis set was used to modelled the influence of electron withdrawing group and electron donating group attached to the dienophile on the kinetics and thermodynamic parameters to show the influence on activation parameters. The calculation indicates that electron withdrawing group (NO_2-substituted dienophile) lowers the activation parameters and thereby increasing the rate of the reaction as observed with lower rate constant, k value compared with unsubstituted and OH-substituted dienophile.

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