



Substituent Effects on Simple Diels-Alder Reactions: Evidence for Possible Explosive Reactions from Quantum Mechanical Calculations

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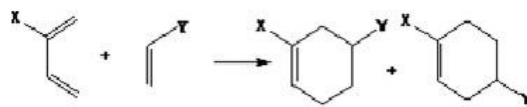
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Abstract

Nature of substituents influences the feasibility of reaction. Electron withdrawing or electron donating substituents on either diene or dienophile results in the decrease or increase in the feasibility of simple Diels Alder reaction involving 1,3-butadiene and ethene. In this paper the feasibility of several Diels Alder reactions having substituted diene and dienophile is calculated in terms of enthalpy of reaction. The way the substituents affect the rate of the reaction can be rationalized with the aid of the frontier molecular orbital theory. The pathway of reaction (normal or inverse electron demand) is predicted by means of HOMO-LUMO energy gap. Normal electron demand Diels Alder reactions are promoted by electron donating substituent on diene and electron withdrawing substituent on the dienophile. In contrast, inverse electron demand Diels Alder reactions are accelerated by electron withdrawing groups on diene and electron donating ones on dienophile. This study helps us to predict the feasibility and path way of certain normal and explosive Diels Alder reactions.



Simple Diels - Alder Reaction

Simple Diels- Alder Reaction always fascinates a synthetic and theoretical chemist equally. Some of such reactions can reach the limit of explosions.

Keywords: DFT, Diels-Alder reaction, inverse electron demand Diels-Alder reaction, explosive reactions.

Introduction

The Diels Alder reaction (in older literature referred to as the “diene synthesis”) is one of the most useful synthetic reactions in organic chemistry. It is a [4 + 2] cyclo

addition reaction in which a molecule with a conjugated -system (a diene) and another with at least one -bond (a dienophile) react to form a cyclohexene derivative (fig: 1), is a powerful tool for the synthesis of six-membered

ring systems. The first example of a Diels-Alder reaction (the dimerization of tetra chlorocyclo penta-dienone) stems from 1892^[1]. The first chemist to identify the importance of the reaction was von Euler in 1920^[2], eight years before the famous paper by Diels and Alder appeared^[3]. Following the explorative work of Diels, Alder and co-workers, the Diels-Alder reaction became an important tool in synthetic organic chemistry.

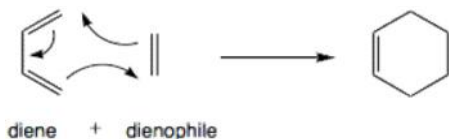


Fig: 1 A simple Diels- Alder Reaction

The way the substituents affect the rate of the reaction can be rationalized with the aid of the frontier molecular orbital theory. This theory was developed during the study of the role of orbital symmetry in pericyclic reactions by Woodward and Hoffmann in 1969^[4] and, independently by Fukui in 1971^[5]. Later, Houk (1975)^[6] contributed significantly to the understanding of the reactivity and selectivity of these processes^[7]. The FMO theory states that a reaction between two compounds is controlled by the efficiency with which the molecular orbitals of the individual reaction partners interact. The interaction is most efficient for those orbitals that overlap best and are closest in energy. The FMO theory further assumes that the reactivity is completely determined by interactions of the electrons that are highest in energy of one of the reaction partners (i.e. those in the Highest Occupied Molecular Orbital, the HOMO) with the Lowest Unoccupied Molecular Orbital (LUMO) of the other partner. Applied to the Diels-Alder reactions, two modes of interaction are possible: the reaction can be controlled by the interaction of the HOMO of the diene and the LUMO of the dienophile (normal electron demand), or by the interaction between the LUMO of the diene and the HOMO of the dienophile (inverse electron demand).

The simple Diels Alder reaction of 1,3-butadiene and ethene is difficult, requiring high temperature and pressure. But has been shown to proceed in a concerted synchronous fashion both experimentally^[8] and theoretically^[9]. The reaction is accelerated by substitution by electron donors on the diene moiety and by the presence of electron-withdrawing substituents on the dienophile^[10]. Many examples of the Diels Alder reaction with the reverse substitution pattern (inverse electron demand Diels Alder) are also known^[11-13]. The reaction proceeds with a high degree of stereo specificity at both diene and dienophile.

The global electrophilicity index proposed by Parr et al.,^[14] has been used to classify dienes and dienophiles, currently used in Diels Alder reactions within a unique scale of electrophilicity. They found that there is a good correlation between the difference in electrophilicity of

the diene and dienophile pair and the feasibility of the cycloaddition. It is the objective of this paper to find out the effect of substituents on the feasibility of simple Diels Alder reaction. We calculate the feasibility of reactions in terms of enthalpy of reaction. Also we predict the path way of all the reactions that we considered. To find out whether a reaction follows normal or inverse electron demand Diels Alder reaction, we calculate the energy difference between the HOMO of the diene/dienophile and LUMO of the dienophile/diene.

Experimental

The present study was conducted using the abinitio and DFT software Gaussian 09 W^[15] software using Gauss View 5.0^[16] on the graphical user interface. GaussView was used to make input files for running in Gaussian 09W. For constructing input files, we draw the skeletal structure of the reactants and products of the various Diels Alder reaction (fig: 2). At first we draw the reactants (butadiene, ethylene) and product (cyclohexene) of the basic Diels Alder reaction. i.e., X=H and Y=H

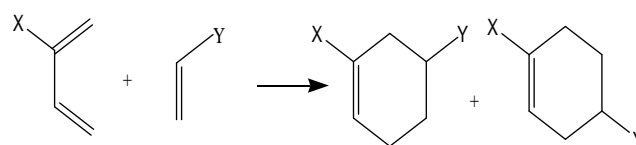


Fig:2 Reaction Scheme

In order to evaluate the effect of substituents, we select four electron donating substituents such as -CH₃, -SiH₃, -OCH₃, -NH₂ and electron withdrawing ones such as -NO₂, -CN, -CHO and -COCH₃. First X is taken as electron donating and Y as electron withdrawing substituents. Then the order is reversed. After that the input file was saved in a gif format and later run in the Gaussian09W initially in AM1 level^[17], which was a molecular mechanics modelling. This was done for getting a guess geometry for the further higher order calculations. The optimized geometry from that level was used as the input for running the next calculation using Hartree-Fock Theory^[18-19] using the STO-3G basis set. Further that optimized geometry was run in HF theory, but using a higher basis set; 6-31G(d). The geometry obtained in that level was in fact used for the calculation using the Density Functional Theory^[20,21] with B3LYP^[22-24] functional and a higher basis set; 6-311G(d)++. During the last run, frequency calculation was performed to analyze vibrational modes of the optimized geometry in order to ensure that there are no imaginary frequencies left in the structure to make sure that the optimized structure was a minima. Pop=full was also requested in the last run, which provides the population of electrons in their orbitals for a detailed analysis if required. The energy obtained was in atomic units. Later they are converted to kJ/mol to get a real life picture.

Results and Discussion

The present study is conducted using B3LYP method with 6-311G++ basis set. Here we are elucidating the effect of electron donating and electron withdrawing substituents on both the diene and dienophile.

Simple Diels- Alder Cyclo-addition between butadiene and ethene

The optimized energies of the 1,3- butadiene and ethene using B3LYP theory and 6-311G++ basis sets are present in the table-1

Diene	Dienophile	Product	H in kJ/mole
1,3 butadiene	Ethene	cyclohexene	
-409559	-206347	-616059	-153.1

Table-1 Energies (kJ/mole) of diene dienophile and product of simple Diels Alder reaction

Diene	Energy	Dienophile	Energy	Energy gap
1,3butadiene	HOMO -644.586505	Ethene	LUMO -24.915995	619.671
	LUMO -115.25945		HOMO -740.28598	855.545

Table-2 Energies (kJ/mole) of HOMO and LUMO of diene and dienophile

It can be inferred that the heat of reaction obtained from the simple homodesmotic equations of the Diels Alder cycloaddition of 1,3-butadiene and ethene is -153.0976808 kJ/mol. The HOMO-LUMO energy gap (table-2) indicates that the reaction follows normal electron demand Diels Alder reaction. One of the major characteristics of the Diels Alder reactions is that Highest Occupied Molecular Orbital (HOMO) of the diene and the Lowest Unoccupied Molecular Orbital (LUMO) of the dienophile or LUMO of the diene and HOMO of the dienophile must have matching molecular orbital (MO) symmetry. This means that in a Diels Alder reaction electrons can flow both ways. On one hand, the diene (1,3-butadiene) is an electron donor and the dienophile (ethene) is an electron acceptor. On the other hand the diene is the electron acceptor and dienophile being an electron donor.

Effect of Electron Donating substituents on diene and Electron Withdrawing substituents on dienophile

Electron donating substituents such as $-CH_3$, $-NH_2$, $-SiH_3$ and $-OCH_3$ are introduced in the diene and $-NO_2$, $-CN$, $-CHO$ and $-COCH_3$ are taken as the

electron withdrawing substituents in the dienophile. The optimized energies of diene dienophile and product (cyclohexene derivative) were found out and are tabulated in the table-3

The experimental data illustrates that the EDG on the diene increases the HOMO energy of the diene and EWG decreases the LUMO energy of the dienophile. This will result in the decreased HOMO-LUMO energy gap and which in turn causes the increase in the feasibility of the reaction. But our calculations prove that feasibility of Diels Alder reaction is not only depend upon the HOMO-LUMO energy gap but also on several other factors. Reactions of $-NO_2$ substituted dienophile with $-CH_3$, $-SiH_3$ and $-NH_2$ substituted diene are energetically more feasible than the simple Diels Alder reaction. All the remaining reactions are with favourable negative H value. But are less negative than the simple Diels Alder. Even though the HOMO-LUMO energy gaps for these reactions are lesser than the simple Diels Alder reaction, they are less feasible energetically. The pathway of electron flow is determined by analyzing the HOMO-LUMO energy gap in table-4. All reactions follow normal electron demand Diels Alder reaction.

Substituents in diene (kJ/mole)	Substituents in dienophile (kJ/mole)	Product (kJ/mole)	H in kJ/mole
CH_3 -512785.8698	NO_2 -743232.6618	1,3	
		1,4	-167.4916721
	CN -448515.8603	1,3	-1256186.023
		1,4	-1256185.426
	CHO -503868.6317	1,3	-166.8943183
		1,4	-961453.5875
		1,3	-151.8574235
		1,4	-961454.6831
		1,3	-152.9530184
		1,4	-1016789.95
		1,3	-135.4480222
		1,4	-1016789.561
		1,3	-135.0598945
		1,4	

	COCH ₃	1,3	
	-607109.2525	-1120029.463	-134.3409801
		1,4	
		-111981.6165	-134.3409801
SiH ₃	NO ₂	1,3	
-1172758.164	-743232.6618	-1916158.464	-167.6375974
		1,4	
		-1916160.048	-169.2216666
	CN	1,3	
	-448515.8603	-1621426.276	-152.2518261
		1,4	
		-1621423.469	-149.444589
	CHO	1,3	
	-503868.6317	-1676760.181	-133.3846943
		1,4	
		-1676761.983	-135.1872313
	COCH ₃	1,3	
	-607109.2525	-1780008.13	-140.7130161
		1,4	
		-1780006.968	-139.5512586
NH ₂	NO ₂	1,3	
-554903.8027	-743232.6618	-1298299.429	-162.9649688
		1,4	
		-1298301.995	-165.5306336
	CN	1,3	
	-448515.8603	-1003564.924	-145.2611435
		1,4	
		-1003569.359	-149.6956655
	CHO	1,3	
	-503868.6317	-1058902.618	-130.1840785
		1,4	
		-1058906.055	-133.621068
	COCH ₃	1,3	
	-607109.2525	-1162145.413	-132.3576774
		1,4	
		-1162152.15	-139.0952618
OCH ₃	NO ₂	1,3	
-710236.929	-743232.6618	-1453611.154	-141.5632843
		1,4	
		-1453613.237	-143.646461
	CN	1,3	
	-448515.8603	-1158877.997	-125.2075745
		1,4	
		-1158858.863	-106.0739282
	CHO	1,3	
	-503868.6317	-1214219.294	-113.7337457
		1,4	
		-1214224.296	-118.7351394
	COCH ₃	1,3	
	-607109.2525	-1317469.05	-122.8686741
		1,4	
		-1317465.115	-118.9332859

Table-3 Energies (kJ/mole) of EDG substituted diene, EWG substituted dienophile and product

Substituents in diene	Energy	Substituent in dienophile	Energy	Energy gap
CH ₃	HOMO - 632.43044	NO ₂	LUMO -351.55445	280.876
	LUMO -92.822425		HOMO -829.369195	736.5578
	HOMO - 632.43044	CN	LUMO -192.527915	439.9025
	LUMO -92.822425		HOMO -789.46706	705.6556
	HOMO - 632.43044	CHO	LUMO -235.638625	396.7918
	LUMO -92.822425		HOMO -720.06963	627.2582
	HOMO - 632.43044	COCH ₃	LUMO -207.20446	425.226
	LUMO -92.822425		HOMO - 692.370605	599.5592
SiH ₃	HOMO -664.19899	NO ₂	LUMO -350.215445	313.983545
	LUMO -114.708095		HOMO -829.369195	714.6611
	HOMO -664.19899	CN	LUMO -192.527915	471.671075
	LUMO -114.708095		HOMO -798.46706	683.758965
	HOMO -664.19899	CHO	LUMO -235.638625	428.560365
	LUMO -114.708095		HOMO -720.06963	605.361535
	HOMO -664.19899	COCH ₃	LUMO -207.20446	456.99453
	LUMO -114.708095		HOMO -692.370605	577.66251
NH ₂	HOMO -539.43523	NO ₂	LUMO -350.215445	189.2198
	LUMO -80.18277		HOMO -829.369195	749.1864
	HOMO -539.43523	CN	LUMO -192.527915	346.9073
	LUMO -80.18277		HOMO -798.46706	718.2843
	HOMO -539.43523	CHO	LUMO -235.638625	303.7966
	LUMO -80.18277		HOMO -720.06963	639.8869
	HOMO -539.43523	COCH ₃	LUMO -207.20446	332.2308
	LUMO -80.18277		HOMO -692.370605	612.1878
OCH ₃	HOMO -602.788545	NO ₂	LUMO -350.215445	252.5731
	LUMO -110.00845		HOMO -829.369195	719.3607
	HOMO -602.788545	CN	LUMO -192.527915	410.2606
	LUMO -110.00845		HOMO -798.46706	688.4586
	HOMO -602.788545	CHO	LUMO -235.638625	367.1499
	LUMO -110.00845		HOMO -720.06963	610.0612
	HOMO -602.788545	COCH ₃	LUMO -207.20446	395.5841
	LUMO -110.00845		HOMO -692.370605	582.3622

Table-4 Energies (Kj/mole) of HOMO and LUMO of diene and dienophile

Effect of Electron Withdrawing Groups on diene and Electron Donating Groups on dienophile

The diene is substituted with electron withdrawing substituents and dienophile with electron donating ones. The optimized energies of reactants and products are depicted in table-5

Among the 16 reactions, energetically more feasible reactions are those with -NO₂ substituted diene and CH₃ and SiH₃ substituted dienophile. The HOMO_{diene} – LUMO_{dienophile} energy gap of these reactions are greater than the simple Diels alder, but the LUMO_{diene} – HOMO_{dienophile} energy gap is lesser. Hence the HOMO of the dienophile acts as the electron donor

and LUMO of the diene as the electron acceptor. These reactions follow an inverse electron demand Diels Alder reaction. Also reactions of -OCH₃ substituted dienophile shows a high negative H value. The reactions may be an explosive reactions. Explosive nature of these reactions cannot be explained only on the basis of HOMO-LUMO energy gap. The reason behind these type of reactions must be further studied. All other reactions show a favourable negative enthalpy but are less feasible than the simple Diels Alder. The feasibility of reactions cannot be explained on the basis of HOMO-LUMO energy gap, which is influenced by other factors also.

Substituents in diene	Substituents in dienophile	Product	H in kJ/mole
NO ₂	CH ₃	1,3	
-946440.4656	-309576.984	-1256181.56	-164.1106582
		1,4	
		-1256176.685	-159.2358136
	SiH ₃	1,3	
	-969551.0058	-1916145.988	-154.5162673

		1,4	
		-1916146.218	-154.747075
	NH ₂	1,3	
	-351696.4717	-1298270.04	-133.1027681
		1,4	
		-1298270.033	-133.0959943
	OCH ₃	1,3	
	-501763.1629	-1453619.781	-5416.152877
		1,4	
		-1453600.35	-5396.721656
CN	CH ₃	1,3	
-651720.7976	-309576.984	-961450.7539	-152.9722895
		1,4	
		-961450.8697	-153.0880741
	SiH ₃	1,3	
	-969551.0058	-1621420.952	-149.1487476
		1,4	
		-1621421.009	-149.205721
	NH ₂	1,3	
	-351696.4717	-1003544.808	-127.5387297
		1,4	
		-1003544.859	-127.5897694
	OCH ₃	1,3	
	-501763.1629	-1158893.547	-5409.586239
		1,4	
		-1158875.374	-5391.413026
CHO	CH ₃	1,3	
-707078.8449	-309576.984	-1016800.797	-144.9683478
		1,4	
		-1016795.451	-139.6217533
	SiH ₃	1,3	
	-969551.0058	-1676766.25	-136.3996347
		1,4	
		-1676766.057	-136.2059253
	NH ₂	1,3	
	-351696.4717	-1058893.023	-117.7061535
		1,4	
		-1058865.68	-90.36388139
	OCH ₃	1,3	
	-501763.1629	-1214239.704	-5397.696583
		1,4	
		-1214221.015	-5379.007381
COCH ₃	CH ₃	1,3	
-810316.2067	-309576.984	-1120040.597	-147.4062295
		1,4	
		-1120035.582	-142.3912357
	SiH ₃	1,3	
	-969551.0058	-1780006.206	-138.9936287
		1,4	
		-1780006.468	-139.2552335
	NH ₂	1,3	
	-351696.4717	-1162108.202	-95.5238028

		1,4	
		-1162129.8	-117.1219009
	OCH ₃	1,3	
	-501763.1629	-1317479.371	-5400.001667
		1,4	
		-1317461.622	-5382.252316

Table-5 energies (kJ/mole) of EWG substituted diene, EDG substituted dienophile and product

Substituent in diene		Energy	Substituent in dienophile		Energy	Energy gap
NO ₂	HOMO	-736.111435	CH ₃	LUMO	-11.49969	724.6117
	LUMO	-343.179105		HOMO	-690.92658	347.7475
	HOMO	-736.111435	SiH ₃	LUMO	-59.65136	676.4601
	LUMO	-343.179105		HOMO	-743.935425	400.7563
	HOMO	-736.111435	NH ₂	LUMO	-30.19325	705.9182
	LUMO	-343.179105		HOMO	-537.64989	194.4708
HOMO	-736.111435	OCH ₃	LUMO	-21.555355	714.5561	
LUMO	-343.179105		HOMO	-614.025685	270.8466	
CN	HOMO	-720.80477	CH ₃	LUMO	-11.49969	709.3051
	LUMO	-217.312635		HOMO	-690.92658	473.6139
	HOMO	-720.80477	SiH ₃	LUMO	-59.65136	661.1534
	LUMO	-217.312635		HOMO	-743.93542	526.6228
	HOMO	-720.80477	NH ₂	LUMO	-30.19325	690.6115
	LUMO	-217.312635		HOMO	-537.64989	320.3373
HOMO	-720.80477	OCH ₃	LUMO	-21.555355	699.2494	
LUMO	-217.312635		HOMO	-614.025685	396.7131	
CHO	HOMO	-696.17758	CH ₃	LUMO	-11.49969	684.6779
	LUMO	-242.832495		HOMO	-690.92658	448.0941
	HOMO	-696.17758	SiH ₃	LUMO	-59.65136	636.5262
	LUMO	-242.832495		HOMO	-743.935425	501.1029
	HOMO	-696.17758	NH ₂	LUMO	-30.19325	665.9843
	LUMO	-242.832495		HOMO	-537.64989	294.8174
HOMO	-696.17758	OCH ₃	LUMO	-21.555355	674.6222	
LUMO	-242.832495		HOMO	-614.025685	371.1932	
COCH ₃	HOMO	-680.870915	CH ₃	LUMO	-11.49969	669.3712
	LUMO	-222.22232		HOMO	-690.92658	468.7043
	HOMO	-680.870915	SiH ₃	LUMO	-59.65136	621.2196
	LUMO	-222.22232		HOMO	-743.935425	521.7131
	HOMO	-680.870915	NH ₂	LUMO	-30.19325	650.6777
	LUMO	-222.22232		HOMO	-537.64989	315.4276
HOMO	-680.870915	OCH ₃	LUMO	-21.555355	659.3156	
LUMO	-222.22232		HOMO	-614.025685	391.8034	

Table-6 Energies (kJ/mole) of HOMO and LUMO of diene and dienophile

Conclusion

Diels Alder reactions are of two type, normal electron demand and inverse electron demand. Electron donating groups on diene and electron withdrawing groups on dienophile enhances the Normal Diels Alder and electron withdrawing substituents in diene and electron donating ones in dienophile promotes inverse electron demand Diels Alder reaction. Feasibility of Diels Alder reaction is not only depend upon HOMO-LUMO energy gap but also on several other factors. Reactions of -OCH₃ substituted dienophile are

explosive reactions. The reason behind such explosive reactions cannot be explained only on the basis of HOMO-LUMO energy gap. Among the 8 substituents on diene/dienophile -NO₂ substituent has more effect on the feasibility of Diels Alder reaction.

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