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Study of kinetics of cyclic reagents Diels–Alder reaction via modern MO methods

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ABSTRACT

Modern quantitative and qualitative Molecular Orbital (MO) methods were used to test the assumption that during Diels-Alder reaction of a cyclic compound A with cyclopentadiene and with furan gives endo product is the kinetic product and the exo product is the thermodynamic product the reaction product is analyzed and the results are considered in terms of relative energies of the reactants and products of each process and Hammond theory. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Diels Alder reaction;
Hammond theory;
Hartee-Fock method;
Spartan '04;
Abinitio.

INTRODUCTION

The Diels–Alder reaction is an organic chemical reaction (specifically, a cycloaddition) between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system.^[1-3] The reaction can proceed even if some of the atoms in the newly-formed ring are not carbon. If the diene and the dienophile both are cyclic then the exo and endo adduct will formed.

Most commonly, diene bears an electron-releasing group (ERG) and dienophile bears an electron-withdrawing group (EWG). The strongest interaction takes place between HOMO of diene and LUMO of dienophile. Carbons that have the highest coefficients in two frontier orbitals will begin to bond; therefore these carbons will direct the orientation of substituents and thus identity of major product of a Diels-Alder reaction. The HOMO of the diene will donate electron density to the LUMO of the dienophile resulting non-polar transition state and cyclic product. In the case of reaction between two

cyclic compounds the transition state follows the endo reaction path. It is therefore endo product will form faster for those reactions.

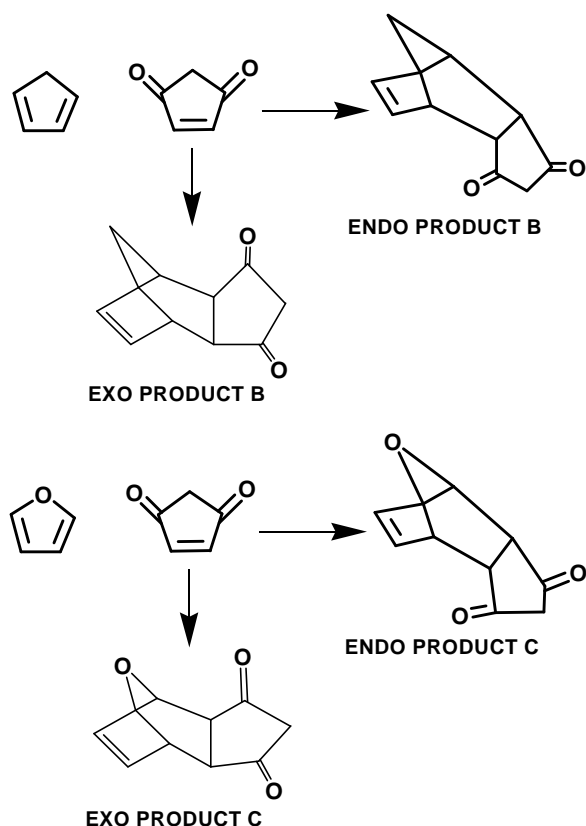
In this report, I tested the hypothesis that the endo product will formed between the reaction of cyclic compound A with cyclopentadiene and furan. Cyclopentadiene and cyclic compound A can react with each other and formed either endo or exo adduct bicyclo [2.2.1] hept-5-ene-cis-2, 3-diketo compound (B). Furan and maleic anhydride can react and formed either exo or endo adduct of 7-oxabicyclo [2.2.1] hept-5-ene-cis-2, 3- diketo compound(C). Using *abinitio* calculation the kinetic and the thermodynamic product of each reaction was predicted and then the two reactions are carried out to test the predictions. The reaction of cyclic compound A with the cyclopentadiene is known to be much faster than that that of furan. The difference in reactivity and the stereochemistry of the adducts formed from the two reactions is considered in terms of relative energies of the reactants, transition states, and products.

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MATERIAL AND METHODS

Molecular modelling and calculation

All calculations were performed using the program Spartan '04 for Windows, from Wave function. Cyclopentadiene, furan, and maleic anhydride were each built and their equilibrium geometry calculated using Hartree-Fock 3-21G* calculations. For each diene, a surface corresponding to the HOMO was generated. For cyclic compound A, a surface corresponding to the LUMO was generated. By visual observation of the overlap of the reactant HOMO and LUMO, a qualitative prediction of the kinetic product of each reaction could be made based on qualitative frontier molecular orbital theory. The ground state energy of each reactant was recorded. The equilibrium ground state energies of the *endo*- and *exo* forms of B and C were then calculated as described above for the reactants. This allowed prediction of the thermodynamic product of each reaction. Considering the energies of the reactants and product for each reaction, a qualitative prediction of the relative positions along the reaction coordinate of the transition states could be made based on the Hammond postulate.



The transition state energy of the predicted kinetic product was calculated for B. Starting with the product structure, the Reaction (curved arrow) module was used to draw arrows representing the retro-Diels-Alder reaction. The energy was then calculated by optimizing the transition state geometry *ab initio* calculations at the 3-21G* level. With the energies of the reactants, transition state and products for the formation of *endo*-B and *endo*-C, it was possible to estimate the relative rates of these two reactions in the forward and the reverse directions (k_1/k_2)_f and (k_1/k_2)_r. This requires the assumption that the entropy of activation (ΔS^\ddagger) of these processes is approximately equal:

thus:

$$\Delta H_B^\ddagger - \Delta H_C^\ddagger \approx \Delta G_B^\ddagger - \Delta G_C^\ddagger = \Delta \Delta G^\ddagger$$

AND

$$K = (K_{B1} T/h) \exp(-\Delta G^\ddagger/RT)$$

$$\text{Hence } K_B/K_C = \exp(-\Delta \Delta G^\ddagger/RT)$$

The reversibility of these two reactions was taken into account when rationalizing the stereochemistry of the isolated products of reactions B and C.

EXPERIMENTAL

TABLE 1 : Calculated energies for the reaction of Cyclopentadiene and compound A

Reaction component	3.21*G energy/Hartrees**	Normalized energy (kJ/mol)
Reactants	-565.8140	162.41108
Endo-transition	-565.7880	230.68959
Endo product (B)	-566.8738	5.798
Exo product (C)	-566.8760	0

**1 Hartree=2625.5 kJmol⁻¹

TABLE 2 : Calculated energies for the reaction of Furan and compound B

Reaction component	3.21*G energy/Hartrees**	Normalized energy (kJ/mol)
Reactants	-602.4463	92.34
Endo-transition	-602.4043	185.09
Endo product (B)	-602.4758	12.03
Exo product (C)	-602.4805	0

**1 Hartree=2625.5 kJmol⁻¹

As per energy calculation it is observed that the endo product dominates in both reactions.

Bicyclo [2.2.1] hept-5-ene-cis-2, 3- diketo compound (B)

In a 50-mL round bottom flask fitted with a dry-

ing tube, cyclic compound A (1.5 g) was added to dry ethyl acetate (5 mL), and the solid dissolved by gentle heating. Diethyl ether (5 mL) was added, and the solution swirled to mix the solvents. The solution was then cooled in an ice bath. Keeping the solution cold, freshly cracked cyclopentadiene (1.2 mL) was added, and the solution swirled (with cooling in an ice bath temp 0 to -5 degree centigrade if necessary) until the exothermic reaction subsided, resulting in a white solid. The crude B was recrystallized *in situ* by gentle heating of the mixture until the solid dissolved, followed by slow cooling of the solution to room temperature to yield large crystals. The crystals were filtered and washed with a small amount of ice-cold ether, and the melting point compared to the known melting points of *endo*-B and *exo*-B.

7-Oxabicyclo [2.2.1] hept-5-ene-cis-2,3-diketo compound (C)

In a 50-mL round bottom flask fitted with a drying tube, cyclic compound A (1.5 g) was added to anhydrous diethyl ether (10 mL), and the solid dissolved by gentle heating. The solution was then cooled in an ice bath, and the volume of ether restored to 10 mL while the solution was still cool, furan (1.0 mL) was added, and the reaction swirled gently. The reaction flask was then stoppered, and the stoppered wrapped in parafilm and secured with a plastic stopper clamp. The reaction was allowed to proceed without stirring for 48 hours. The resulting solid was collected on a Hirsch funnel, and washed with ice-cold hexane (~1 mL). Crude C was recrystallized from hexane-ethyl acetate by heating the solid in hexane (5 mL) until the mixture just reaches boiling, followed by addition of enough warm ethyl acetate to dissolve the solid. The solution was allowed to cool to room temperature and, after crystals had appeared, cooled in an ice bath. The recrystallized C was filtered and washed with ice-cold hexane (2 x 1 mL), and dried. The melting point was compared to the known melting points of *endo*-C and *exo*-C.

Modelling experiment

I have found Spartan '04 for Windows 7 to be relatively straightforward to use. For this experiment, the results generated are consistent, and the recommended level of theory results in processing times of less than three minutes using PCs with INTEL CORE 2 DUO

processors. I have found no advantage to using a higher basis set to calculate the energies of the ground states or transition states. (Single point energy calculations using the 6-31G* basis set on the 3-21G* geometry adds an extra step and up to 3 minutes to each calculation.) A graph of the energies can be used to show the differences in the two processes

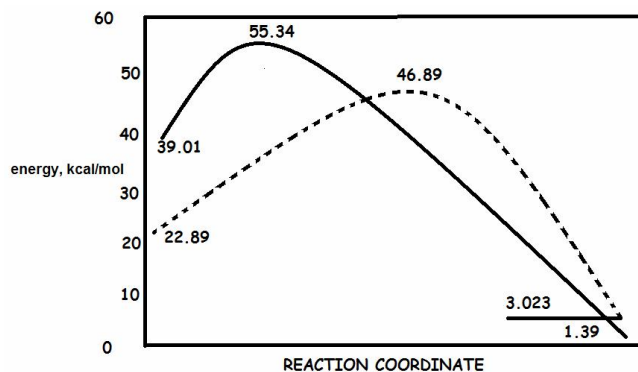
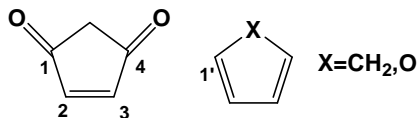


Figure 1 : A graph of the calculated 3-21G* energies of the reactants, transition state and product for the formation of the *endo*-adducts B (-) and C (- -). Position of the transition states along the reaction coordinate has been imposed by the author.

Note that this graph, while illustrative, should be treated only as an illustration, and not a means of calculating absolute activation energies. Electron correlation methods (such as MP2 calculations or pBP density functional methods) are necessary to account for reaction energetics accurately. Hartree-Fock methods are only satisfactory in describing relative activation energies. Regarding the geometry of the transition states, it is instructive to examine the CYCLIC COMPOUND A moiety of the activated complex leading to *endo*-B and that leading to *endo*-C. For each reaction, the dihedral angles defined by the exocyclic carbon, carbon 1/4, carbon 2/3, and hydrogen 2/3 change from 0° for CYCLIC COMPOUND A to about 58° in the product (58.5° for *endo*-B, 58.7° for *endo*-C). In the activated complex leading to *endo*-C, this dihedral angle is 23.4°, 5.9° greater than that found in the transition state leading to *endo*-B. Other measures of the position of the transition state along the reaction pathway, such as the length of the new bond forming between carbon 2 and carbon 1', are consistent with a later transition state in the reaction with furan.

Observation of the vibrational modes of the activated complex is a useful exercise in that it demon-

TABLE 3



EXO CARBON

Feature	Reaction	Transition state	Product
C2—C1'	B	2.21 Å	1.57
C2—C1'	C	2.13	1.57
H2-C2-C1-Cexo	B	17.5°	57.5
H2-C2-C1-Cexo	C	23.4°	56.7°

strates that a single imaginary frequency is present that corresponds to the reaction coordinate.

However, this calculation is much more time consuming than transition state geometry optimizations. In the case of the transition state leading to *endo*-C, INTEL CORE PROCESSOR the 3-21G* transition state energy calculation required less than 3 minutes, while the frequency calculation took over 40 minutes using a INTEL CORE PROCESSOR.

Product melting points (calculated in a MEL-TEMP 3.0 melting point apparatus.) (From the Dictionary of Organic Compounds, 6th edition, Chapman & Hall, Electronic Publishing Division, 1996)

- *endo*-B 138 °C (product B)
- *exo*-B 154-156 °C (product B)
- *endo*-C 78-80 °C (product C)
- *exo*-C 124 °C (product C)

CONCLUSION

This experiment will prove presumption that the *endo* adduct is dominate as the figure suggests the chief production of the *endo* adduct.

ACKNOWLEDGEMENT

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