

C343 Experiment IV

Diels Alder Reaction

1 Effect of EWG on Dienophiles

To Study the effect of Electron withdrawing groups(EWG) on dienophiles, acrylonitrile base is chosen and more cyano groups are added step by step. The equilibrium geometries for acrylonitrile, 1,1-dicyanoethylene, cis- and trans-1,2-dicyanoethylene, tricyanoethylene, and tetracyanoethylene using the HF/3-21G level of theory were obtained. The Results along with experimental log(rates) are as follows:

S.No	Molecule	LUMO Energy(Hartree)	log(rate)
1	Acrylonitrile	0.10464	0
2	1,1-dicyanoethylene	0.05155	4.64
3	Cis-1,2-dicyanoethylene	0.04265	1.94
4	Trans-1,2-dicyanoethylene	0.04002	1.89
5	Tricyanoethylene	-0.00435	5.66
6	Tetracyanoethylene	-0.04558	7.61

As we know, addition of EWG lowers the LUMO energy of the molecule. So as we increase the number of cyanide groups, the LUMO energy must decrease. Hence we expect the nature of graph to decreasing which is what we observe in figure 1.

Now, we also expect the rates of reaction to be higher as the LUMO energy decreases (as it comes more closer to HOMO leading to a better overlap). So, a plot of LUMO energy vs log(rate) must be decreasing. In figure 2 we can see it follows trend mostly, but at 4.64 we can see a increase in energy corresponding to 1,1-Dicyanoethylene. The points at 4.64,1.94,1.89 correspond to molecules with two CN groups, only their positions are different. For 4.64 its 1,1-Dicyanoethylene and 1.94,1.89 are cis and trans 1,2-Dicyanoethylene. So, 1,1-Dicyanoethylene is more reactive(higher rate) than its 1,2 counterparts this is due to former transition state(1,1) having a distortion only on one end compared to distortion on both sides for latter TS(1,2). Hence, making TS(1,1) more lower in energy than TS(1,2) leading to a higher rate. The cis and trans have almost equal rates. So, **eventhough 1,1-Dicyanoethylene doesn't reduce LUMO energy much, it increases the reaction rate than 1,2-Dicyanoethylene due to stable TS.**

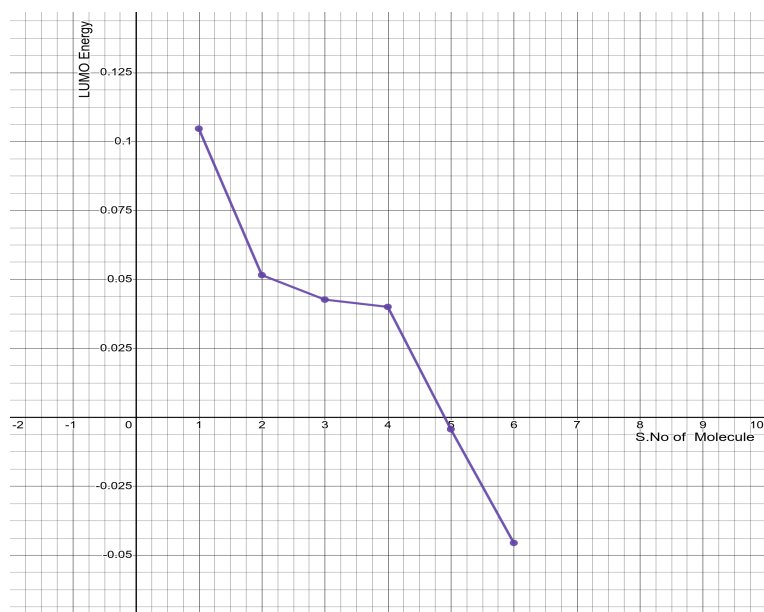


Figure 1: Plot of LUMO Energy for different molecules vs S.No of molecules



Figure 2: Plot of LUMO Energy for different molecules vs log(rates)

2 Transition State and Activation Energy Calculation

The transition-state geometries for Diels-Alder cycloadditions of acrylonitrile and cyclopentadiene and tetracyanoethylene and cyclopentadiene was obtained

using the HF/3-21G level of theory. The Results are as follows:

Molecule	Imaginary Frequency	Electronic Energy (EE) + G_{corr} (Hartree)
Cyclopentadiene	-	-191.643469
TS1	-692.04	-360.368847
TS2	-533.35	-634.005964
Acrylonitrile	-	-168.790540
Tetracyanoethylene	-	-442.409856

Activation Energy(ΔG^\ddagger) calculation for both TS

$$\Delta G^\ddagger = \Sigma(E E + G_{corr})_{TS} - \Sigma(E E + G_{corr})_{Reactant}$$

(i) Activation Energy of TS1

$$\begin{aligned}\Delta G^\ddagger(\text{TS1}) &= -360.368847 - (-191.643469 - 168.790540) \\ &= 0.065 \text{ Hartree} \\ &= 170.657 \text{ kJ/mol}\end{aligned}$$

(ii) Activation Energy of TS2

$$\begin{aligned}\Delta G^\ddagger(\text{TS2}) &= -634.005964 - (-191.643469 - 442.409856) \\ &= 0.047 \text{ Hartree} \\ &= 123.398 \text{ kJ/mol}\end{aligned}$$

The Rate of a reaction can be calculated by:

$$k(T) = \frac{k_b T}{h c_0} e^{-\Delta G^\ddagger / RT}$$

$$k_1 = 0.37425 \cdot 10^{34} \exp(-170.657 \cdot 1000 / (8.314 \cdot 298)) = 0.455 \cdot 10^4 \text{ s}^{-1}$$

$$\begin{aligned}k_2 &= 0.37425 \cdot 10^{34} \exp(-123.398 \cdot 1000 / (8.314 \cdot 298)) = 0.876 \cdot 10^{12} \text{ s}^{-1} \\ \text{So, Relative Rates} &= k_2/k_1 = 1.925 \cdot 10^8\end{aligned}$$

Therefore, theoretical difference in log(relative rates) = 8.28

The experimentally observed difference in log(relative rates) = 7.61

Thus, the experimental and theoretical value are in pretty close agreement. And adding more EWG indeed lowers the LUMO energy, TS barrier height leading to a faster reaction rate. Hence, Tetracyanoethylene has a higher rate than acrylonitrile with cyclopentadiene.