

Computational Study of Gas Phase Aromatic Nucleophilic Substitution of Phenoxy in 2, 4-Dinitrodiphenylether with Dimethylamin

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Abstract: - Nucleophilic aromatic substitution of phenoxy from 2,4-dinitrodiphenylether with dimethylamin was carried out in the gas-phase using theoretical methods; semi-empirical PM6, density functional theory B3LYP/6-31G* and hartreefock HF/3-21G. Calculations were done for the reactants and transition states in which the properties of the system are known and parameters such as the Entropy, Enthalpy and Gibb's free energy were calculated for both the reactant and the product and their change evaluated. The reaction follows a second order kinetics and all methods gave a good fit for Arrhenius Equation indicating that as the temperature rises, the specific rate constant increases accordingly. All the methods gave negative values of ΔS , density functional gave the most negative value for change in entropy, semi-empirical PM6 has the highest value for activation energy but the lowest value of rate constant arising from the high value of Gibb's free energy, Hartreefock gave the highest values for both pre-exponential factor and the rate constants. The rate of reaction is temperature dependent but not feasible at temperatures below room temperature.

Keywords:- Nucleophilic substitution; rate constants; temperature

I. INTRODUCTION

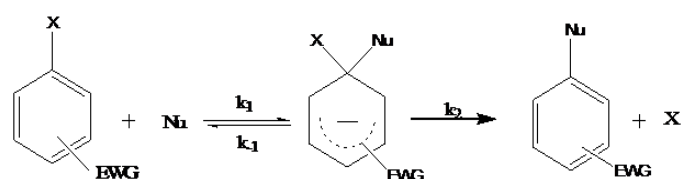
Aromatic substitution reaction is a type of aromatic reaction in which the substituent of the aromatic system is being substituted by an incoming Nucleophilic. The aromatic substrate is susceptible to the attack due to the strong pi bond, so the aromatic ring is activated by a strong electron withdrawing group such as NO₂, COPh, and MeCO₃ at the ortho and/or Para positions. Aromatic Nucleophilic substitution reactions using amines are an important class of organic reactions having synthetic applications and continue to inspire studies related to its kinetics [2].

Studies have revealed that the displacement of the substituent at 1- position is faster when the aromatic ring contains electron-withdrawing substituents at ortho and Para positions [6]. The effect of electron-withdrawing substituents and solvents on the rate of the displacement of fluoride, chloride or phenoxy group at position-1 by primary and secondary amines has been the subject of many investigations [3,7]. Most of the reports on kinetic measurements agree that the reaction is second order (equation (i)), first order with respect to the substrate and first order with respect to the

amine, and the rate determining step is the formation of the activated complex [5,6].

$$\text{Rate of reaction} = k [\text{substrate}] [\text{Nucleophilic}] \dots\dots\dots (I)$$

Most aromatic substitution reactions occur through intermediate complex mechanism which can generally represented by the reaction below.



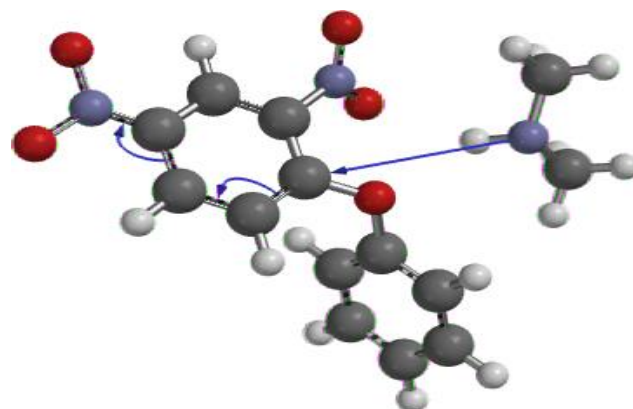
Scheme 1: General mechanism of aromatic Nucleophilic substitution reaction.

Herein, we report the aromatic Nucleophilic substitution of phenoxy in 2,4-dinitrophenylether (i.e. the substrate) having NO₂ as the electron withdrawing substituent at ortho- and Para- positions, while the amine being dimethylamine.

II. METHODOLOGY

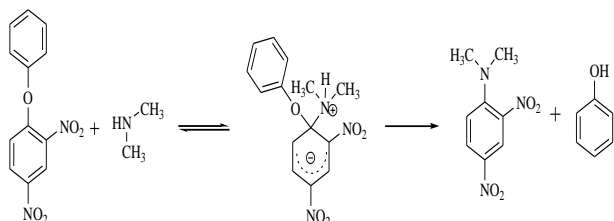
The substrate and the amine for the study were modeled using the SPARTAN'14 program

(<https://www.wavefun.com/products/spartan.html>) Graphical User Interface (GUI). Following this was a guess transition state (TS) to illustrate the mechanism of the reaction (sheme2).



Scheme 2: Mechanism of reaction for the formation of activated complex (transition state)

Transition State Geometry (TSG) and Equilibrium Geometry calculations were then carried out on the TS structure and the reactants respectively; each evaluating thermodynamics parameters such as enthalpy, entropy and Gibb’s free energy.



Scheme 3: Mechanism of reaction for the Nucleophilic aromatic substitution of phenoxy in 2,4-dinitrodiphenylether with dimethylamine.

All calculations were carried out in the gas phase using semi-empirical Parameterized Method Six (PM6), Hatreefock 3-21G and Density Functional Theory (DFT) B3LYP/6-31G* methods. The difference between the values of transition state and reactant for the aforementioned parameters were used to evaluate the rate of the reaction at different temperatures of 288K, 298K, 302.9K, 308K and 313K.

III. RESULTS AND DISCUSSIONS

The difference between the values of the transition state (ts) and reactants (r) for the thermodynamic parameters, entropy, enthalpy and Gibb’s free energy, were evaluated using the following relationships respectively.

$$\Delta S = S_{ts} - S_r \dots\dots\dots (II)$$

$$\Delta H = H_{ts} - H_r \dots\dots\dots (III)$$

$$\Delta G = G_{ts} - G_r \dots\dots\dots (IV)$$

Temperature (K)	ΔS (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
288.0	-0.01600	24.62250	29.2162
298.0	-0.01637	24.54375	29.4000
302.9	-0.01654	24.49125	29.5050
308.0	-0.01666	24.46500	29.6100
313.0	-0.01670	24.43875	29.6625

Table 1:- Thermodynamic parameters calculated with B3LYP/6-31G

Temperature (K)	ΔS (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
288.0	-0.00059	12.6262	19.7925
298.0	-0.00030	12.6525	12.7312
302.9	-0.00016	12.6262	12.6787
308.0	-0.00004	12.6525	12.6525
313.0	-0.00003	12.6525	12.6787

Table 2:- Thermodynamic parameters calculated with HF/3-21G

Temperature (K)	ΔS (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)
288.0	-0.00631	84.0121	-85.8293
298.0	-0.00634	83.9957	-85.8847
302.9	-0.00690	83.9905	-85.9103
308.0	-0.00633	83.9963	-85.9459
313.0	-0.00632	84.0001	-85.9762

Table 3:- Thermodynamic parameters calculated with PM3

The entropy measure the degree of disorderliness of a system, the negative ΔS indicates that the entropy decreases as we move from the reactants to the transition states and the entropy increases generally with increasing temperature.

The rate constant for the formation of activated complex has been calculated using the equation:

$$k = k^* \times \frac{K_B T}{h} \dots\dots\dots (V)$$

$$k^* = e^{-\frac{\Delta G^\ddagger}{RT}} \dots\dots\dots (VI)$$

So the rate constant can be calculated by combining the two equations above to give

$$k = \frac{K_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \dots\dots\dots (VII)$$

Where K_B is the Boltzmann constant, h is the plank’s constant, R is molar gas constant. Tables I – III show the ΔS, ΔG and ΔH of the three methods used at different temperatures.

The dependence of the rate constant of a reaction on temperature can be expressed by this equation, now known as the Arrhenius equation:

$$k = A e^{-\frac{E_a}{RT}} \dots\dots\dots (VIII)$$

In which E_a is the activation energy of the reaction (in kilojoules per mole), R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), T is the absolute temperature, and e is the base of the natural logarithm scale. Taking the natural logarithm of both sides, we have:

$$\ln k = \ln A - \frac{E_a}{RT} \dots\dots\dots (IX)$$

When compared with the equation of a straight line graph, ($y = mx + c$), $\ln k$ was plotted against $1/T$ which gave a straight line graph, where the slope is $-E_a/RT$ and the intercept is $\ln A$. The values of activation energy, E_a and the pre-exponential factor A were therefore calculated from the graph.

Rate Constants were measure in $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$

Temperature (K)	PM6	HF	DFT
288.0	1.621E-3	2.861E10	3.008E7
298.0	3.355E-3	3.620E10	4.352E7
302.9	9.002E-3	4.058E10	5.141E7
308.0	16.992E-3	4.556E10	6.092E7
313.0	29.154E-3	5.057E10	7.298E7

Table 4:- The values of rate constants at different temperatures

a) Activation energy (E_a) = 8.661×10^7 J/mol

b) Pre-exponential factor (A) = 8.31×10^{12}

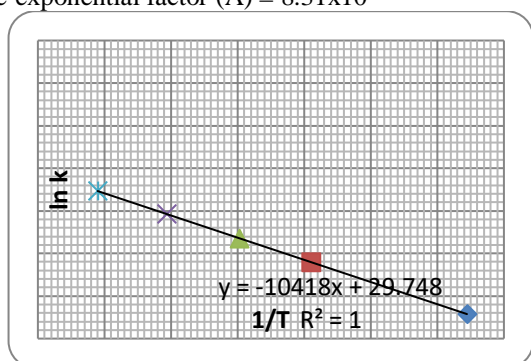


Fig 1:- Graph of $\ln k$ against $1/T$ using semi-empirical PM6 method

a) Activation energy (E_a) = 1.7211×10^7 J/mol

b) Pre-exponential factor (A) = 3.77×10^{13}

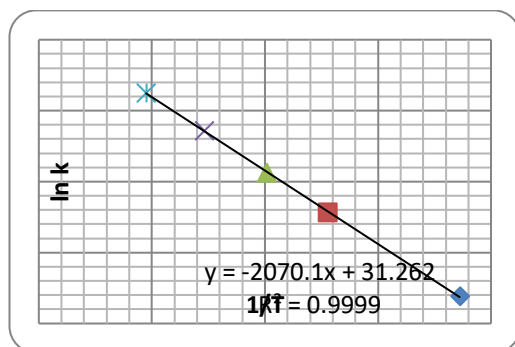


Fig 2:- Graph of $\ln k$ against $1/T$ using Hartree-Fock method (3-21G)

a) Activation energy (E_a) = 2.6387×10^7 J/mol

b) Pre-exponential factor (A) = 1.83×10^{12}

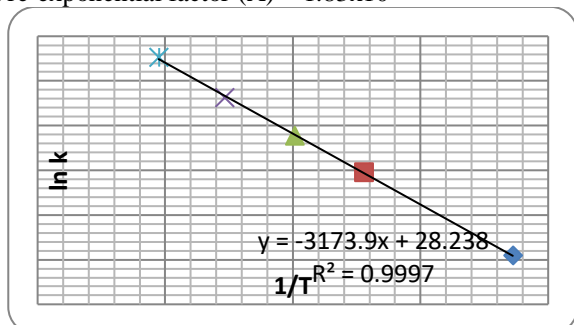


Fig 3:- Graph of $\ln k$ against $1/T$ using DFT method B3LYP/6-31G*

IV. CONCLUSION

The theoretical studies of aromatic Nucleophilic substitution with an amine has been carried out, the phenoxy group of 2,4-dinitrodiphenylether was substituted for where the reaction was investigated in the gas phase. The reaction is second order overall in which case the formation of the transition state is the rate determining step. The rate of reaction is fit with Arrhenius equation and it increases with temperature and the spontaneity of the reaction which is dependent on ΔG is negative showing that the reaction is spontaneous.

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