

## Investigation of unimolecular reaction for C–H and N–H bonds fission in aniline by calculation Arrhenius parameters with RRKM method and analysis of NBO and HOMO, LUMO orbitals

Z. Heidarneshad\*, M. Vahedpour

<sup>1</sup> Department of Chemistry, University of Zanjan. P.O. Box 45371-38791, Zanjan, Iran.

Submitted March 24, 2016; Accepted August 8, 2016

The present study provides quantitative results for the rate of unimolecular Carbon–Hydrogen and Nitrogen–Hydrogen bonds fission reaction of Aniline (AN) at elevated temperatures up to 2000 K. The potential energy surface for each C–H bond fission reactions (in the Ortho, Meta and Para positions) and N–H bond fission reactions of Aniline were investigated using abinitio calculations. The geometry and vibrational frequencies of the species involved in these reactions were optimized at the MP2 level of theory, using the cc–pVDZ basis set. Since C–H bond fission channel is a barrier less reaction, it has been used variational RRKM theory to predict rate constants. By means of calculated rate constant at different temperatures, the activation energy and exponential factor were determined. The Arrhenius expression for C–H bond fission reaction of Aniline on the Ortho, Meta and Para sites and N–H bond fission reaction are obtained as:  $k(T)_{Ortho} = (1.6E16)Exp(-54347.92/T)$ ,  $k(T)_{Meta} = (5.9E17)Exp(-57899.44/T)$ ,  $k(T)_{Para} = (3.4E17)Exp(-59336.96/T)$ ,  $k(T)_{N-H} = (2.2E21)Exp(-48298.29 /T)$  respectively. Moreover, the effect of Amino group nucleophilic attraction and resonance with Benzene ring, molecular rotation, natural charge, natural bond orbital (NBO), HOMO, LUMO orbital energies and tunneling effect on the rate expression have been discussed.

**Keywords:** Aniline, Unimolecular Reaction, variational RRKM, Bonds Fission.

### INTRODUCTION

Aniline (Aminobenzene) is used as an intermediate in the preparation of a gamut of chemicals and materials [1] and also reacts easily in the blood to convert hemoglobin into methaemoglobin, thereby preventing oxygen uptake [2]. Consequently, the wastewaters containing significant levels of aromatic amines is needed to be treated before they are discharged into the environment because of their high toxicity potential mentioned–above. Conventional methods for the removal or destruction of Aniline from wastewaters include solvent extraction, biodegradation [3], catalytic oxidation [4], membrane separation [5–7], ultrasonic degradation [8], supercritical water oxidation [9], and electrochemical oxidation [10]. Conducting polymers which are soluble in water are more important and versatile, with regards to applications, than those soluble in organic solvents [11]. Regardless of their lower conductivity, these substituted polyanilines are drawing significant attention [12–20] as they are soluble and processable. The aim of this work is to consider the C–H bond fission reaction of aniline followed to investigation on effect of different substitutions in the benzene ring on the above mentioned reaction. Although every molecule can undergo many

different reactions but also computational chemistry provides the possibility of investigation on a single channel alone. Calculation of different potential energies such as reaction and formation Enthalpies involve large errors. However quantum mechanical consideration of bond fission reaction may be expected to involve small error, because in this type of reactions, the number and the type of basis sets remains among the reactant and also in product. It may be noted that bond fission reactions almost belong to isodesmic reactions because of similar bonding on both sides of the equation.

### COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 09 suites of programs [21]. Fully optimized geometries, harmonic frequencies, the zero point vibrational energy (ZPVE) of the involved molecules were calculated with the second–order Møller– Plesset perturbation theory (UMP2) using the Dunning’s correlation consistent polarized valence double  $\zeta$  basis set denoted as cc–pVDZ [22]. The optimized geometry of Aniline is depicted in Fig. 1. According to Eq.1,  $k(E)$  was calculated for energies up to  $100000\text{ cm}^{-1}$  above the ground state energy, including the zero point energy.

Regarding to  $\nu$ RRKM criteria, the value of  $k(E)$  is accepted at energies which  $k(E)$  values were minimum with respect to the reaction coordinate variations (see Eq. 2). Fig. 2 and Fig. 4 shows that the C–H<sub>Ortho</sub> and N–H bonds fission reaction occur

\* To whom all correspondence should be sent:

E-mail: .heidarneshad@gmail.com

when the reaction coordinate for C–H<sub>Ortho</sub> is more than 2.81 Å and is less than 3.01 Å depending on the energy.

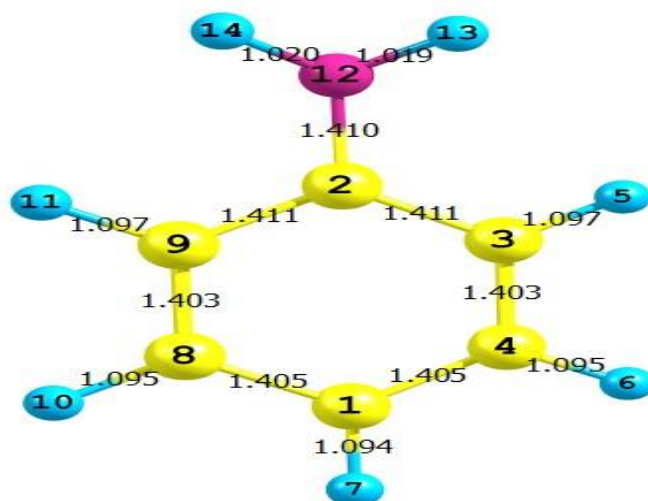


Fig. 1. Optimized geometry of Aniline. Bond lengths are in Å.

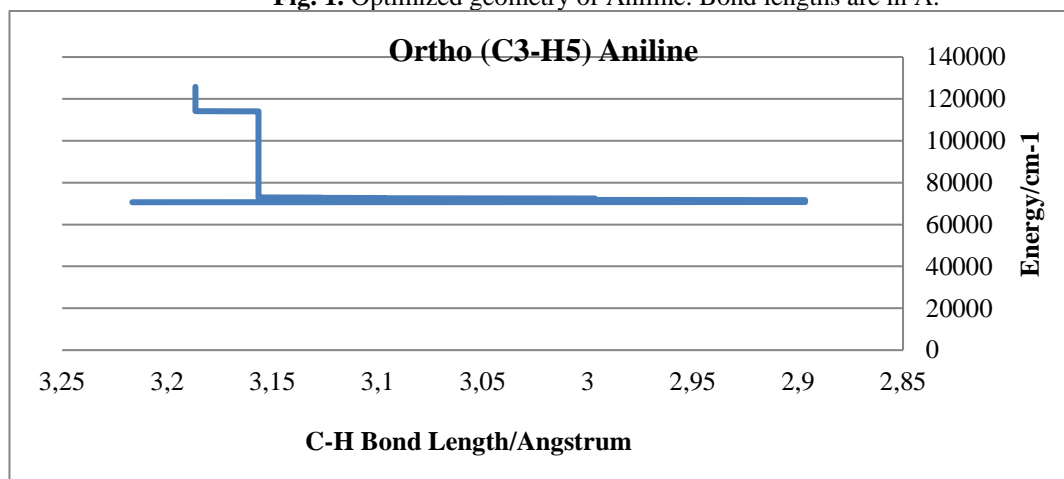


Fig. 2. The transition state C3–H5 bond length in terms of transition state available energy.

The length of designated C–H and N–H bonds for fission is considered as a reaction coordinate for corresponding reaction. In each separate optimization, the length of intended C–H and N–H bonds are increased gradually (0.1 Å each time) and the energy of molecule is minimized regarding to all molecular structural variables except the reaction coordinate. Then, molecule was kept in the minimum energy pass on the potential energy surface through the C–H and N–H bonds. At each point on the minimum energy pass, vibrational frequencies were calculated. The calculations have been carried out in the range of energy from  $E_0$  (The energy of transition state which is corrected for ZPVE) to 100000  $\text{cm}^{-1}$  above the energy of the ground state which is corrected for ZPVE. According to RRKM theory the micro canonical energy dependent rate constant is calculated from the following formula.

$$k(E) = \frac{\sigma G^{++}(E - E_0)}{h\rho(E)} \quad (1)$$

Where  $E_0$  stands for the energy of the saddle point on the potential energy surface (Corrected for ZPVE),  $G^{++}(E - E_0)$  denote the number of energy states for Orthogonal modes to the reaction coordinate at the transition state configuration with energy equal or less than  $E - E_0$ ,  $h$  is plank constant,  $\sigma$  stands for the degeneracy of reaction and  $\rho(E)$  stands for the density of states of ground state molecule with energy equal to  $E$  (Corrected for ZPVE). When a saddle point along the reaction path exists, it represents a ‘bottleneck’ between product and reactants. It is the point along the reaction coordinate where we have the smallest rate of transformation from the reactant to products. This can be seen from Eq. 1, where it should be noted that only the sum of states  $G^{++}(E - E_0)$  changes as the

reaction proceeds along the reaction coordinate. Due to the lack of distinct saddle point along the reaction coordinate on the potential energy surface for bond fission reactions studied in this investigation, it has been used the variational *RRKM* (*vRRKM*) criteria to obtain the transition state structures [23–30]. Thus, in *vRRKM* theory the rate constant, that is,  $k(E)$  in Eq. 1, is calculated as a function of the reaction coordinate, and the minimum identifies the activated complex.

$$\frac{\partial G^{++}(E-E_0)}{\partial R_c} = 0 \quad \text{Or} \quad \frac{\partial k(E)}{\partial R_c} = 0 \quad (2)$$

Moreover, the available energy for breaking C–H<sub>Ortho</sub> and N–H bonds of Aniline must be more than 70000 cm<sup>-1</sup>. Evidently in the calculation of  $k(T)$ , the range of  $k(E)$  values is used which verifies the *vRRKM* criteria, that means the range of  $k(E)$  values accepted which becomes minimum with respect to the reaction coordinate variations. Fig. 3 and Fig. 5 has illustrated the variation of  $k(E)$  versus the available energy for C–H<sub>Ortho</sub> and N–H bonds. It shows that the  $k(E)$  values increases as available energy increases, as respected.

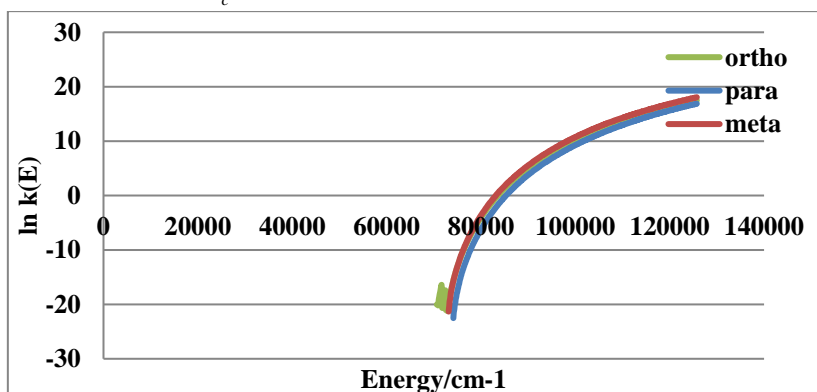


Fig. 3. Microcanonical rate constant for (Ortho, Para and Meta) C–H bond fission pathway of Aniline.

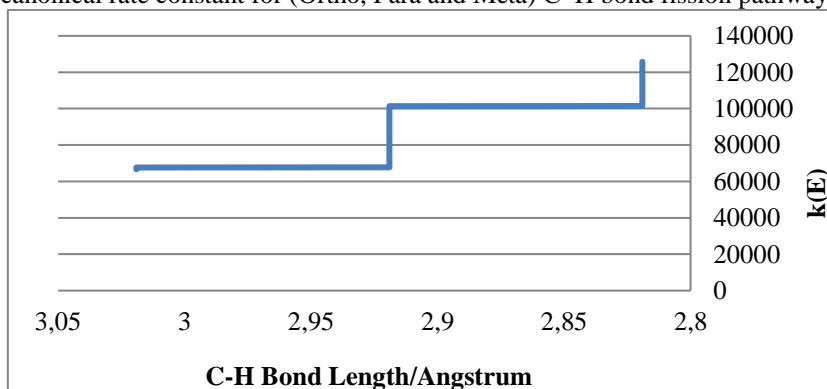


Fig. 4. The transition state N–H bond length in terms of transition state available energy

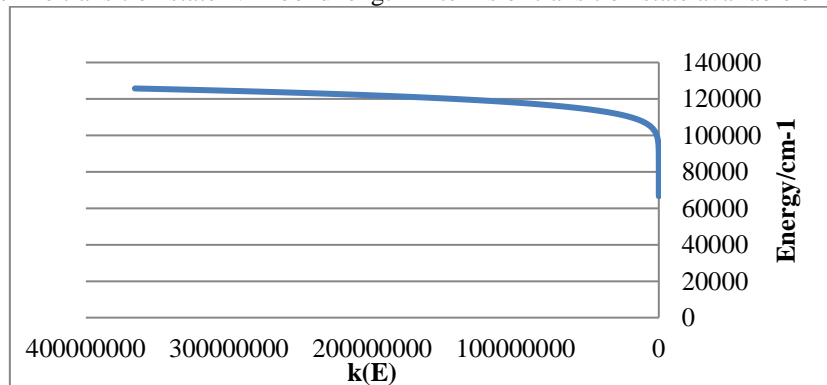


Fig. 5. Microcanonical rate constant for N–H bond fission pathway of Aniline

The canonical reaction rate  $k(T)$ , is calculated by using integration of obtained microcanonical rate constants,  $k(E)$ , over the energies from 0 to 100000 cm<sup>-1</sup> above ZPVE of the ground state.

$$k(T) = \int P(E)k(E)dE \quad (3)$$

In the above equation,  $P(E)$  is the Boltzmann energy distribution function for  $s$  uncoupled harmonic oscillators and rotational motion of the molecule. The Wigner method is applied to estimate

of the tunneling corrections for the reactions [31, 32].

$$\kappa(T) = 1 + \frac{1}{24} \left( \frac{h\nu^{++}}{kT} \right)^2 \quad (4)$$

Where  $\nu^{++}$  is the imaginary frequency of the transition state structure, the activation energy and exponential factor are obtained using plotting of  $\ln k(T)$  versus  $1/T$  according to the well-known Arrhenius equation [33].

## RESULTS AND DISCUSSION

To accurately evaluate  $G^{++}(E - E_0)$  and  $\rho(E)$ , several methods have been suggested. These methods have been implemented in several computer programs [34–35]. Generally, vibrational and rotational densities of states are calculated separately. For vibrational case, due to the large energy level spacing, a very efficient algorithm for direct counting of  $\rho(E)$  and  $G^{++}(E - E_0)$  was introduced by Beyer and Swinehart [36, 37]. It uses only two loops, one over energy with a given grain size and the other over vibrational frequencies for calculating density of states.

The sum of states is obtained using applying summation over density of states. Using Beyer–Swinehart algorithm, all the vibrational density and sum of states lower than specified energy will be evaluated, and we only need to calculate density and the sum of vibrational states at the highest requested energy. The accuracy of this method depends on the grain size of energy loop, if the grain size is chosen as  $1\text{cm}^{-1}$ , this method in fact is as accurate as the direct counting method. Therefore, in this study we have used the grain size equal to  $1\text{cm}^{-1}$ . In this investigation due to small differences in the rotational energy levels of molecules, the rotational number and density of states is calculated classically. Formerly, *RRKM* used to consider kinetically reactions associated to break groups of hydrogens in Benzene, Nitrobenzene and Fluorobenzene molecules [38, 39]. One of the main hypothesis in *RRKM* is that all micro states of vibration and orbiting included equal possibility to occur, but recent investigations showed that although molecular orbits calculated through following equation and classically, results were not confirmed experimental results. Regarding to above equation and closeness of distances between levels of orbiting energy, number of orbiting micro states rather than density of states, showed increasing available energy (Fig. 3), and it revealed much more extents to get kinetically Parameters such as  $K(E)$ . In fact, number of orbiting states than density of

number of orbiting states increased in high pace. Therefore, sever increases in  $k(E)$  and then in  $k(T)$  observed. These increases were irrational in compare to experimental data was experimental results in bond fission of Carbon–Hydrogen of Benzene [40]. Moreover, in reactions such as bond fission change length of bonds, then moments of inertia different from molecules in basic state. The difference cause to change in energy levels associated to orbiting energy. For example, energy levels determine through following equation, and increasing moments of inertia caused to reduce energy in energy levels. Hence, if transition state included much more moments of inertia, energy of transition is lower than energy in basic state. In fact, molecules of transition state consists of lower available energy to move molecules orbital–increasing main quantum number,  $J$  to molecule in basic state than molecules in transition state included much more possibility to be available orbited movements. This is caused to tangible increase in  $k(E)$  and  $k(T)$  though increasing main quantum numbers of  $J$ . In Table 1, Activation energy and exponential factor to bonds fission of Carbon–Hydrogen different conditions in Benzene, Nitrobenzene, Fluorobenzene gathered. Moreover, costs of calculations had severe increases and increases of  $J$ . As pace of process change regards to increase  $J$  from 0 to 1 slightly, calculation of  $k(T)$  was rational for  $J=0$ . According to our previous article and our calculations on benzene and nitrobenzene with calculated date for aniline the Arrhenius parameters for C–H bond fission reaction (Three positions Ortho, Meta and Para) are listed in table 1.

Activation energy for C-H bond fission reaction of aniline for three positions Ortho, Meta and Para are 449.4, 479.3 and 492.2 respectively in terms of  $\text{KJ mol}^{-1}$  and tunneling effect can be reduced  $E_a$  and frequency factor in all positions and by considering the rotational motion of molecule in calculation is increased  $E_a$ . For example, considering the rotational motion for ortho position in aniline is increased  $E_a$  about  $8.4 \text{KJ mol}^{-1}$ . According to table 1, reaction coordinates in C–H bond fission for transition state in three positions of ortho, Meta and Para are respectively. Figure 2 is shown reaction coordination transition state to minimum energy at C-H bond fission for ortho position in aniline. Know that micro canonical rate constants are not minimized in all energies and those are accepted that minimized in available energy. Figure 3 show the rate constants that their available energies is minimized in ortho position and we have better and higher rate constants with increasing available energies. We have three different atoms in benzene ring in aniline due to the

NH<sub>2</sub> substituent that the major difference of them is being their distance from NH<sub>2</sub> substituent. NH<sub>2</sub> and NO<sub>2</sub> have different electron resonance effects on the benzene ring. Comparison between C–H bond fission reaction of ortho position for aniline and nitro benzene show that NH<sub>2</sub> substituent is decreased the activation energy of C–H bond fission about 44 kJ mol<sup>-1</sup> than the activation energy of C–H bond fission in benzene and NO<sub>2</sub> substituent is decreased about 23 kJ mol<sup>-1</sup> but in meta position of NO<sub>2</sub> substituent activation energy is decreased about 14.6 kJ mol<sup>-1</sup> than activation energy of C–H bond fission and NH<sub>2</sub> substituent is about 14.11 kJ mol<sup>-1</sup>. In ortho position resonance effect and electron donor is effective and activation energy is more reduced but in meta position, NO<sub>2</sub> electrophile effect is more efficient and reduces more the activation energy and in para position also NO<sub>2</sub> reduces more. However they have few difference together. Although NH<sub>2</sub> is electron donor and NO<sub>2</sub> is electrophile but both of them have effective in three ortho, meta and para position and the reduce the activation energy of C–H bond fission energy. electron delocalization, resonance of

benzene ring  $\pi$  electrons in Aniline according to NH<sub>2</sub> substituent in ortho position can be seen clearly in area coordinates reaction of C–H bond fission when the bond length reaches at 2.89 Å and until bond length reaches to 2.89 Å (Refer to Table 2, See NBO Data) and these Electron transfer and resonances are not seen in ground structure and bond length coordinate before 2.89. Activation energy of ortho C–H bond fission reaction in aniline is less than Meta position of aniline, this is because renounce of lone pair with  $\pi$  electron of ring and  $\sigma$  belongs to aniline that can be seen as electron delocalization. Also electron resonance of C3–H5 bond (ortho position) is with  $\pi$  and  $\sigma$  electrons of benzene in aniline. Arrhenius expression for C–H bond fission reaction of Aniline on the ortho, Meta and para sites are obtained as:

$$k(T)_{Ortho} = (1.6E16) \text{ Exp } (-54347.92/T)$$

$$k(T)_{Meta} = (5.9E17) \text{ Exp } (-57899.44/T)$$

$$k(T)_{Para} = (3.4E17) \text{ Exp } (-59336.96/T)$$

$$k(T)_{N-H} = (2.2E21) \text{ Exp } (-48298.29/T).$$

**Table 1.** The Arrhenius Parameters for C–H bond breaking reactions in the Aniline (AN), Benzene and Nitrobenzene (NB), all the data printed as bold and italic face ( data for Benzene, Nitrobenzene and Fluorobenzene ) are collected from references 38 and 39 of this article.

		$\sigma$	With Tunneling		Without Tunneling		Transition state C–H bond Length
			<i>E<sub>a</sub></i> /(kJ/mol)	A/Hz	<i>E<sub>a</sub></i> /(kJ/mol)	A/Hz	
Including Rotational Motion	<i>FB–Ortho</i>	2	<b>481.7</b>	<b>2.00E+21</b>	<b>486.6</b>	<b>1.80E+21</b>	<b>2.894</b>
	<i>FB–Meta</i>	2	<b>495.9</b>	<b>6.10E+21</b>	<b>501.1</b>	<b>4.90E+21</b>	<b>2.895–3.195</b>
	<i>FB–Para</i>	1	<b>502.4</b>	<b>2.60E+21</b>	<b>507.5</b>	<b>2.20E+21</b>	<b>2.894–3.294</b>
	<i>Benzene</i>	6	<b>463.6</b>	<b>6.90E+20</b>	<b>471.5</b>	<b>8.10E+20</b>	<b>3.095–3.395</b>
	<i>NB–Ortho</i>	2	<b>441.4</b>	<b>9.60E+19</b>	<b>449.9</b>	<b>1.10E+20</b>	<b>2.89–3.09</b>
	<i>NB–Meta</i>	2	<b>448.5</b>	<b>8.20E+19</b>	<b>456.7</b>	<b>9.30E+19</b>	<b>3.1–3.3</b>
	<i>NB–Para</i>	1	<b>450.9</b>	<b>1.60E+19</b>	<b>458.6</b>	<b>1.90E+19</b>	<b>3.19</b>
	<i>AN–Ortho</i>	2	456.8	5.50E+20	461.8	4.90E+20	2.89–3.15
	<i>AN–Meta</i>	2	484.4	2.20E+22	489.5	1.80E+22	3.15–3.45
	<i>AN–Para</i>	1	496.9	1.20E+22	501.3	1.00E+22	3.14–3.45
<i>AN–N–H</i>	2	406.99	2.18E+21	411.95	1.9E+21	2.8–3.019	
Excluding Rotational Motion	<i>FB–Ortho</i>	2	<b>476.6</b>	<b>6.10E+16</b>	<b>481.6</b>	<b>5.50E+16</b>	<b>2.894</b>
	<i>FB–Meta</i>	2	<b>491.2</b>	<b>1.80E+17</b>	<b>496.4</b>	<b>1.50E+17</b>	<b>2.895–3.195</b>
	<i>FB–Para</i>	1	<b>495.5</b>	<b>1.30E+17</b>	<b>500.7</b>	<b>1.00E+17</b>	<b>2.894–3.294</b>
	<i>Benzene</i>	6	<b>493.4</b>	<b>2.00E+18</b>	<b>498.5</b>	<b>1.70E+18</b>	<b>3.095–3.395</b>
	<i>NB–Ortho</i>	2	<b>470.4</b>	<b>2.10E+17</b>	<b>475.7</b>	<b>1.60E+17</b>	<b>2.89–3.09</b>
	<i>NB–Meta</i>	2	<b>478.78</b>	<b>2.10E+17</b>	<b>483.97</b>	<b>1.70E+17</b>	<b>3.1–3.3</b>
	<i>NB–Para</i>	1	<b>478.84</b>	<b>3.30E+16</b>	<b>484.01</b>	<b>2.80E+16</b>	<b>3.19</b>
	<i>AN–Ortho</i>	2	449.9	1.60E+16	455.06	1.30E+16	2.89–3.15
	<i>AN–Meta</i>	2	479.3	5.90E+17	484.46	5.00E+17	3.15–3.45
	<i>AN–Para</i>	1	491.2	3.40E+17	496.3	2.80E+16	3.14–3.45
	<i>AN–N–H</i>	2	401.5	6.3E+16	406.5	5.6E+16	2.8–3.019

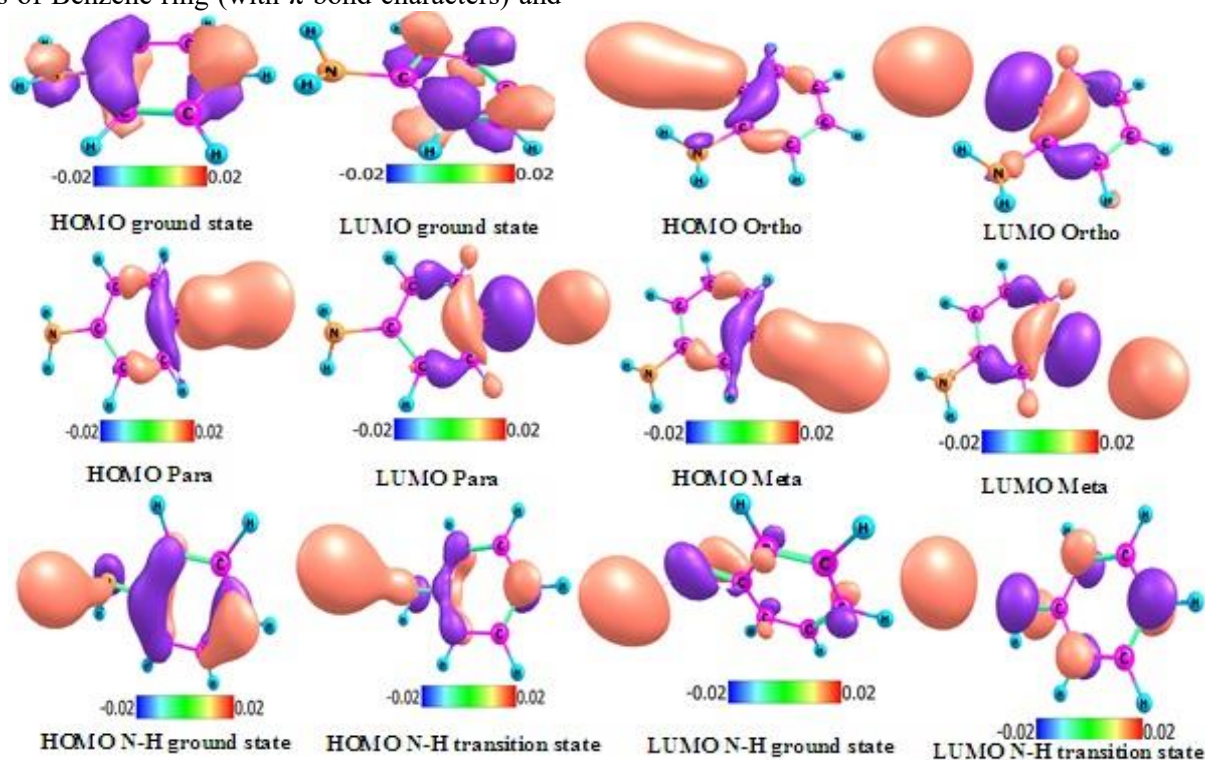
**Table 2.** E2 energies for reaction coordinate of ortho position in Aniline.

Donor NBO (i)→ Acceptor NBO (j)	E2 (kcal/Mol)
$\pi^*_{C2-C9} \rightarrow \pi^*_{C1-C8}$	596.94
$\pi^*_{C1-C8} \rightarrow \pi^*_{C3-C4}$	263.66
$\pi^*_{C2-C9} \rightarrow \pi^*_{C3-C4}$	204.98
$\pi_{C1-C8} \rightarrow \pi^*_{C2-C9}$	38.4
$\pi_{C1-C8} \rightarrow \pi^*_{C3-C4}$	36.82
$\pi_{C2-C9} \rightarrow \pi^*_{C3-C4}$	37.98
$\pi_{C3-C4} \rightarrow \pi^*_{C2-C9}$	43.18
$\pi_{N12} \rightarrow \sigma^*_{C3-H5}$	2.5
$LP^*_{N12} \rightarrow \pi^*_{C2-C9}$	22.2
$LP^*_{N12} \rightarrow \pi^*_{C2-N12}$	2.7
$LP^*_{N12} \rightarrow \sigma^*_{C3-H5}$	37.86
$\sigma^*_{C3-C5} \rightarrow \pi^*_{C1-C4}$	1.2
$\sigma^*_{C3-C5} \rightarrow \pi^*_{C2-C9}$	0.98
$\sigma^*_{C3-C5} \rightarrow \pi^*_{C3-C4}$	0.74
$\sigma^*_{C3-C5} \rightarrow \sigma^*_{C4-H6}$	0.62

Here, quantum mechanical descriptor changes have been investigated in accordance to reaction coordinate. Results from this approach were compared to those from RRKM. In this study, quantum mechanical descriptor value related to HOMO and LUMO orbitals were calculated. We have tried to use these Parameters to describe transition state and to describe intermolecular reactions. It's necessary to note that VRRKM is a time-consuming method, thus it would be useful to replace it with quantum mechanical descriptor to predict transition state. HOMO orbital is formed as a linear combination of Pz orbitals from nitrogen and carbon atoms (see Fig. 6), and spreads on over both sides of Benzene ring (with  $\pi$  bond characters) and

on the nitrogen atom. LUMO orbital is made by linear combination of Pz orbitals from C3, C4, C8 and C9 atoms, each contributing equally (see Fig.6) and shows  $\pi^*$  bond characteristics.

As C3–H5 bond length increases up to 1.69 Å no change is observed, but when it reaches 1.69 Å, LUMO orbital is formed mainly through linear combination of Py orbitals from C3 atom(in greater extent) and s orbital from H5 atom(lower extent) and shows  $\sigma^*$  bond characters. Notably, as C3–H5 bond length increases, s orbital from H5 atom becomes the driving counterpart, progressively, (see Fig.6) It is more interesting when C3–H5 bond length increases beyond 2.69 Å.

**Fig. 6.** HOMO and LUMO orbitals structure for ortho position and N-H bond in Aniline.

In this case, HOMO orbital is formed mainly by s orbital from H5 atom. So it can be concluded that according to variations seen in the HOMO and LUMO orbitals as reaction proceeds, one can say C3–H5 bond is broken only when its bond length reaches 2.69 Å and becomes greater than it. This conclusion is consistent with the predicted transition state bond length in Table 3. A similar situation is seen in the C1–H7 bond fission reaction. As long as bond length is not greater than 1.6 Å, everything is still same as ground state. When bond length reaches 1.7 Å LUMO orbital changes so that it is mainly formed through linear combination of s orbitals from H7 atom and Px from C1 atom and s orbitals

from C4 and H8 atoms (with lower contributions), representing  $\sigma^*$  characters, see Fig.6. This situation maintained until bond length reaches 2.4 Å. when bond length reaches 2.5 Å, the essence of HOMO changes so that it is formed through linear combination of s orbital from H7 atom and Px orbital from C1 atom, representing characteristics of  $\sigma$  bond between C1 and H7 atoms, as shown in Fig.6. There is any variation until bond length reaches 3.4 Å. As C1–H7 bond length increases until to 3.05 Å the HOMO orbital remains without any change but LUMO is stabilized mainly from s orbital on the H7 atom.

**Table 3.** HOMO and LUMO orbitals energy at Ortho position in all reaction coordinate ( $R_c$ ) for Aniline.

Ortho (C3–H5)			Meta (C4–H6)			Para (C1–H7)		
$R_c$	HOMO	LUMO	$R_c$	HOMO	LUMO	$R_c$	HOMO	LUMO
1.0966	-0.2935	0.1352	1.0954	-0.2935	0.1352	1.09432	-0.29349	0.13521
1.1966	-0.2943	0.135	1.1536	-0.2944	0.1351	1.1432	-0.29411	0.13436
1.2966	-0.2953	0.1345	1.2536	-0.2953	0.1348	1.2432	-0.29517	0.13303
1.3966	-0.2964	0.1338	1.3536	-0.2965	0.1342	1.3432	-0.29644	0.13161
1.4966	-0.298	0.1327	1.4536	-0.2978	0.1333	1.4432	-0.29797	0.13001
1.5966	-0.2997	0.1313	1.5536	-0.2994	0.1322	1.5432	-0.29975	0.12822
1.6966	-0.3016	0.1216	1.6536	-0.3011	0.122	1.6432	-0.30177	0.12475
1.7966	-0.3037	0.1048	1.7536	-0.3029	0.1053	1.7432	-0.30398	0.1084
1.8966	-0.3059	0.0886	1.8536	-0.3048	0.0891	1.8432	-0.30633	0.09247
1.9966	-0.3081	0.0733	1.9536	-0.3069	0.0739	1.9432	-0.30878	0.07737
2.0966	-0.3104	0.0592	2.0536	-0.3089	0.0598	2.0432	-0.31127	0.06325
2.1966	-0.3127	0.0461	2.1536	-0.3109	0.0467	2.1432	-0.31377	0.05014
2.2966	-0.3149	0.0339	2.2536	-0.3128	0.0344	2.2432	-0.31603	0.03778
2.3966	-0.317	0.0226	2.3536	-0.3147	0.0234	2.3432	-0.31837	0.02661
2.4966	-0.3187	0.012	2.4536	-0.3148	0.013	2.4432	-0.31327	0.01627
2.5966	-0.3123	0.002	2.5536	-0.3066	0.0034	2.5432	-0.30529	0.00621
2.6966	-0.3051	-0.0074	2.6536	-0.2996	-0.0062	2.6432	-0.29801	-0.0032
2.7966	-0.2986	-0.0163	2.7536	-0.293	-0.015	2.7432	-0.29142	-0.012
2.8966	-0.2927	-0.0248	2.8536	-0.2871	-0.0233	2.8432	-0.2855	-0.0204
2.9966	-0.2873	-0.0329	2.9536	-0.2817	-0.0312	2.9432	-0.28019	-0.0284
3.0966	-0.2823	-0.0407	3.1536	-0.2771	-0.0388	3.1432	-0.27543	-0.036
3.1266	-0.2873	-0.0329	3.2536	-0.2728	-0.0461	3.2432	-0.27116	-0.0433
3.1566	-0.2794	-0.0453	3.3536	-0.269	-0.0529	3.3432	-0.26733	-0.0502
3.1866	-0.2502	-0.0381	3.4536	-0.2656	-0.0595	3.4432	-0.26385	-0.0568
3.2166	-0.2497	-0.04	3.5536	-0.2625	0.2032	3.5432	-0.26064	-0.0632
3.2466	-0.2492	-0.0419	–	–	–	–	–	–
3.2766	-0.2486	-0.0437	–	–	–	–	–	–
3.3066	-0.2481	-0.0454	–	–	–	–	–	–
3.3366	-0.2475	-0.0470	–	–	–	–	–	–
3.3666	-0.2470	-0.0487	–	–	–	–	–	–
3.3966	-0.2466	-0.0504	–	–	–	–	–	–
3.4266	-0.2462	-0.0520	–	–	–	–	–	–
3.4566	-0.2457	-0.0533	–	–	–	–	–	–

Then from the view point of variations seen in the HOMO and LUMO it can be said that the reaction is occurred when the C1–H7 bond length is increased from 3.05 Å. The C4–H6 and N12–H13 bond fission reactions are showed the same results. Although HOMO in ground state spreads it's electron density

on both sides of the aromatic ring in steady state and represents conjugated  $\pi$  bond characteristics, but as bond length increases, it acts like a breaking  $\sigma$  molecular orbital in the breaking C–H bond. Increase in bond length, results in progressive increase in contribution of orbital P from carbon

atom and orbital s from detaching hydrogen atom. Only for C3–H5 bond, the transition state could be determined by monitoring sudden alterations in the linear combination of the orbitals participating in HOMO (see Fig.7). This could not be applied to N12–H13, C1–H7, C3–H5 bonds, as gradual variations in the linear combination of atomic orbitals participating in the HOMO are observed, but considering the linear combination of atomic orbitals in the HOMO is still of significant importance in determination of the transition state location. Ground state LUMO orbital is formed of Pz orbitals from

carbon atoms in the aromatic ring and represents  $\pi^*$  bond characteristics. Increase in length of the breaking C–H or N–H bond causes LUMO to gain the role of  $\sigma^*$  bond in the breaking C–H or N–H and also results in increased contribution of p orbitals from carbon or nitrogen atom and S orbital from the rolled hydrogen atom. Usually, one of the orbitals s in hydrogen atom or p orbitals in carbon atom can allocate the most contributions, eventually. And LUMO orbital is finally formed from one of these two orbitals (This bond length is similar to observed bond length in transition state).

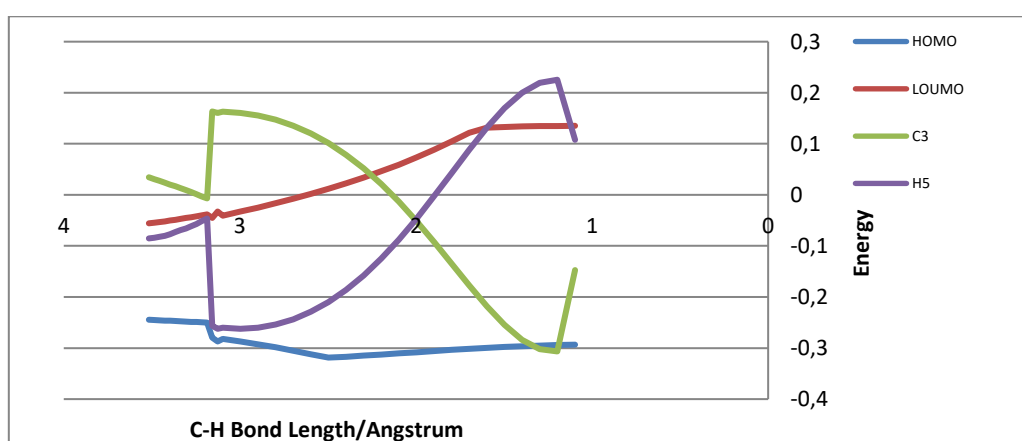


Fig. 7. HOMO, LUMO, C3 and H5 orbitals energy of transition state at ortho position in Aniline.

## CONCLUSION

NH<sub>2</sub> substituent reduces the activation energy of C–H bond fission reaction on Benzene ring. Activation energies of C–H bond fission reaction for three positions (Ortho, Meta and Para) in Aniline are 449.9, 479.3 and 491.2 respectively in terms of kJ mol<sup>-1</sup>. Therefore activation energy is less in ortho position. Activation energy of N–H bond fission reaction is lower than the activation energy of C–H bond fission reaction in aniline, Benzene, Fluorobenzene and Nitrobenzene. So, N–H bond fission reaction develops sooner in competition with C–H bond fission reaction. Tunneling effect can be reduced activation energy and high change in frequency factor at three positions (Ortho, Meta and Para) in Aniline but by applying rotational motion of molecule activation energy is increased in calculation and considering the rotational motion of molecule in calculation. Through checking orbitals energy LUMO, HOMO and atomic charges, in Ortho position the greatest impact occurs from NH<sub>2</sub> the high proportion can be detected from bond coordinate of C–H bond fission. By investigation natural bond orbital (NBO), resonance and electron delocalization also can be recognized by transition state bond length for C–H bond fission in ortho position.

## REFERENCES

1. L. Schmerling, *U.S. Patent*, **2**, 948-755(1960).
2. M.F. Khan, P.J. Boor, B.S. Kaphalia, N.W. Alcock, G.A.S. Ansari, *Fund. Appl. Toxicol.*, **25**, 224(1995).
3. F.J. O'Neill, K.C.A. Bromley–Challenor, R.J. Greenwood, J.S. Knapp, *Water Res.*, **34**, 4397(2000).
4. J.J. Barbier, L. Oliviero, B. Renard, D. Duprez, *Catal. Today*, **75**, 29 (2002).
5. F. Pithan, C. Staudt–Bickel, R.N. Lichtenthaler, *Desalination*, **148**, 1(2002).
6. R. Devulapalli, F. Jones, *J. Hazard. Mater.*, **70**,157 (1999).
7. S.R. Jadhav, N. Verma, A. Sharma, P.K. Bhattacharya, *Sep. Purif. Technol.*, **24**, 541 (2001).
8. Y. Jiang, C. P'etrier, T.D. Waite, *Ultrason. Sonochem.*, **9**, 163(2002).
9. X.H. Qi, Y.Y. Zhuang, Y.C. Yuan, W.X. Gu, J. *Hazard. Mater.* **90**, 51 (2002).
10. E. Brillias, J. Casado, *Chemosphere*, **47**, 241 (2002).
11. J. Yue, A.J. Epstein, *J. Am. Chem. Soc.*, **112**, 2800 (1990).
12. J.M. Ginder, A.F. Richter, A.G. Macdiarimid, A.J. Epstein, *Solid State Commun.*, **63**, 97 (1987).
13. H.S.O. Chan, S.C. Ng, W.S. Sim, K.L. Tan, B.T.G. Tan, *Macro molecules*, **25**, 6029 (1992).
14. J. Yue, A.J. Epstein, *J. Am. Chem. Soc.*, **112**, 2800 (1990).
15. C. Dearmit, S.P. Armes, J. Winter, F.A. Uribe, S. Gottesfeld, C. Mombourquette, *Polymer*, **11**, 2794(1993).



16. M.T. Nguyen, P. Kasai, J.L. Miller, A.F. Diaz, *Macromolecules*, **27**, 3625 (1994).
17. M. Angelopoulos, N. Patel, J.M. Shaw, *Mater. Res. Soc. Symp. Proc.*, **328**, 173 (1994).
18. J.M. Liu, J.H. Hwang, S.C. Yang, *Mater. Res. Soc. Symp. Proc.*, **247**, 601 (1992).
19. S.A. Chen, G.W. Hwang, *J. Am. Chem. Soc.* **11**, 10055 (1995).
20. M. Angelopoulos, N. Patel, J.M. Shaw, N.C. Labianca, S.J. Rishton, *Vac. Sci. Technol.* **11**, 2794(1993).
21. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. *Gaussian, Inc., Wallingford CT.* (2009).
22. T.H. Dunning Jr, *J. Chem. Phys.*, **90**, 1007 (1989).
23. E.D. Glendening, J.K. Badenhop, A.E. Reed, J. E. Carpenter, J.A. Bohmann, C.M. Morales, F. Weinhold, NBA (Univ. of Wisconsin, Madison, WI), Version 5.0(2001).
24. E.P.Z. Wigner, *Phys. Chem.*, **B19**, 203 (1932).
25. N.E. Henriksen, F.Y. Hansen, *Phys. Chem. Chem. Phys.*, **4**, 5995 (2002).
26. L. Masgrau, A. González-Lafont, J.M. Lluch, *Theor. Chem. Accounts*, **110**, 352 (2003).
27. W.P. Hu, G.C. Lynch, Y.P. Liu, I. Rossi, J.J., Stewart, R. Steckler, V.S. Melissas, *Computer Phys. Commun.*, **88**, 344 (1995).
28. D.H. Lu, T.N. Truong, V.S. Melissas, G.C., Lynch, Y.P. Liu, B.C. Garrett, *Computer Phys. Commun.*, **71**, 235 (1992).
29. S.H. Mousavipour, V Saheb. *Bull. Chem. Soc. Japan*, **80**, 1901 (2007).
30. S.H. Mousavipour, M Sadeghi. *Bull. Chem. Soc. Japan*, **89**, 681 (2016).
31. S.J. Klippenstein, *J. Chem. Phys.* **96**, 367 (1992).
32. N.E. Henriksen, F.Y. Hansen., *Phys. Chem. Chem. Phys.*, **4**, 5995 (2002).
33. L. Masgrau, A. Gonzalez-Lafont, J.M. Lluch., *Theor Chem Acc*, **110**, 352 (2003).
34. Hu, W. P., Lynch, G. C., Liu, Y. P. et al., *Computer Phys. Commun.*, **88**, 344 (1995).
35. D.H. Lu, T.N. Truong, V.S. Melissas, et al., *Computer Phys. Commun.*, **71**, 235 (1992).
36. Stein, S. E., Rabinovitch, B. S., *J. Phys. Chem*, **58**, 2438(1973).
37. T. Beyer, D. Swinehart, *Commun. ACM*, **16**, 379 (1973).
38. A.T. Manesh, Z. Heidarneshad, N. Masnabadi, *Russian J. Phys. Chem. A*, **87**, 1175 (2013).
39. A.T. Manesh, Z. Heidarneshad, M. Vahedpour, N. Masnabadi, *Progress in Reaction Kinetics and Mechanism*, **42**, 1 (2017).
40. See NIST Website.