

## Analysis of the reaction kinetics of aminotoluene molecule through DFT method

B. Eren, Y. Yalcin Gurkan \*

Namik Kemal University, Department of Chemistry, Tekirdag / Turkey

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In this study, the most probable reaction paths of aminotoluene (o-toluidine) molecule with OH radical were analyzed. The optimized geometry was calculated via Gauss View 5. Subsequently, the lowest energy status was found out through geometric optimization via Gaussian 09 programme. The geometric structure analysis and bond lengths were also calculated. This study aims to determine the most probable path for the product distribution of aminotoluene and OH radical interaction in gas phase and aqueous media. Quantum mechanical methods were used to indicate the impact of reaction rate over primary intermediate, hydroxylated intermediate, and finally the impact of water solvent.

With the aim to determine the intermediates occurring at the reaction of aminotoluene degradation, geometric optimization of the reactant and transition status complexes were realized through Density Functional Theory (DFT) method. Based on the Quantum mechanical calculation, all probable rate constants of reaction paths were calculated by using Transition Status Theory (TST). For the determination of the transition status of the reaction, C-O bonds were taken as reference. Activation energy for probable reaction paths of all transition status complexes, and their most stable state were calculated from the thermodynamic perspective for the gas phase and aqueous media. The impact of water solvent was investigated by using COSMO as the solvation model.

Key words: Aminotoluene, hydroxyl radical, DFT calculation, TST, COSMO

### INTRODUCTION

Volatile aromatic compounds constitute a major part of air and water contaminants. They are mainly emitted into the environment from anthropogenic sources such as combustion processes, vehicle emissions and industrial sources, as well as from biogenic processes [1,2]. Organic contaminants exist at very low concentrations in water [3]. Therefore, it is essential that the organic contaminants be removed from drinking water [4]. Natural purification of water systems such as rivers, creeks, lakes, and pools is realized by solar light on earth. Sunbeams initiate the degradation reaction of big organic molecules into smaller and basic molecules, finally providing the formation of CO<sub>2</sub>, H<sub>2</sub>O, and other molecules [5, 6].

In its reactions with organic molecules, OH behaves as an electrophile whereas O is a nucleophile. Thus, OH readily adds to unsaturated bonds while O does not. Both forms of the radical abstract H from C-H bonds and this can result in the formation of different products when the pH is raised to a range where O rather than OH is the reactant. For example, if an aromatic molecule carries an aliphatic side chain, O attacks there by H abstraction whilst OH adds preferentially to the aromatic ring [7]. Hydroxyl radical which is the most reactive type known in biological systems

reacts with every biomolecule it encounters including water. Potentially, every biomolecule is a hydroxyl radical scavenger at different speeds [8]. Aromatic compounds are good detectors since they hydroxylate. In addition, the position of attack to the ring depends on the electron withdrawal and repulsion of previously present substituents. The attack of any hydroxyl radical to an aromatic compound results in the formation of a hydroxylated product [9].

While an intermediate in aminotoluene herbicide synthesis is used in the production of more than 90 paints and pigments, rubber, chemicals and pesticides, it is also used as a hardening agent for epoxy resin systems, a reactive material for the glucose analysis and fibre dying in clinic laboratories [10]. Due to the damaging effects of living organisms emitting resistant bad smell, and because of their solubility, aminotoluenes and their derivatives constitute an important water contaminant group. Although many methods are available for the removal of these molecules from water, every method has its own inconvenience [10-13].

In this study, the kinetics of the degradation reaction of aminotoluene and hydroxyl derivatives was analyzed theoretically. With the aim to determine the intermediates obtained from the reaction of aminotoluene degradation, geometric optimization of the reactant and transition status

\* To whom all correspondence should be sent:  
E-mail: yyalcin@nku.edu.tr

complexes were realized through the Density Functional Theory (DFT) method. Based on the quantum mechanical calculation, all probable rate constants of reaction paths were calculated by using Transition Status Theory (TST).

## COMPUTATIONAL SET-UP AND METHODOLOGY

### *Computational models*

The molecular models were created by using the mean bond distances, the geometric parameters of the benzene ring, tetrahedral angles for  $sp^3$ -hybridized carbon and oxygen atoms, and  $120^\circ$  for  $sp^2$ -hybridized carbon atoms. In the calculation of the hydroxylated radicals, the aromatic ring was left planar except for the position of attack. The attacking  $\bullet OH$  radical was assumed to form a tetrahedral angle with the C–H bond due to the change in the hybridization state of the carbon at the addition center from  $sp^2$  to  $sp^3$  [2].

### *Molecular Orbital Calculations*

It is possible that in the photocatalytic degradation reactions of organic contaminants, more harmful products may occur than in the original material. Therefore, before experimentally realizing a photocatalytic degradation reaction, it is essential to know what the primary intermediate products are. The most reliable and accurate information is gathered through calculations carried out with quantum mechanical methods. Thus, since the yield produced is the same, the photocatalytic degradation reaction of o-toluidine and its hydroxy derivatives is based on the direct reaction of these molecules with the OH radical.

With this aim, the kinetics of the reactions of aminotoluene and aminotoluene derivatives with OH radicals was theoretically analysed. The study was initiated with aminotoluene and then exposed to OH radical reaction, and the reaction of the yield was modeled at the gas phase. The experimental findings in the scientific literature show that OH radicals detach hydrogen atom from saturated hydrocarbons, and OH is added to unsaturated hydrocarbons and materials of aromatic structure [14]. For this purpose, all possible reaction paths for the analysed reactions were determined, for every reaction path, molecular orbital calculations of reactant, yield, transition state complexes were carried out with the density function theory (DFT), their molecular orbital calculations were realized and their geometries were optimized.

### *Kinetic Data Treatment*

**The aim** of this study was to develop a model providing the outcome of the yield distribution of the photocatalytic degradation reactions. The vibration frequencies, the thermodynamic and electronic features of every structure were calculated using the obtained optimum geometric parameters. Afterwards, the rate constant and activation energy of every reaction was calculated using the Transition State Theory for a temperature of  $25^\circ C$  based on the quantum mechanical calculation results.

In order to find out the rate of reaction, it is necessary to calculate the equilibrium constant. The equilibrium constant is calculated using the partition functions according to mechanical methods. If the equilibrium constant  $K^\ddagger$  is written in terms of partition functions, it is as follows:

$$K^\ddagger = \frac{q^\ddagger}{q_A \cdot q_B}, \quad (1)$$

$q^\ddagger$ ,  $q_A$ ,  $q_B$ : partition functions belonging to transition state complex and reactants. Molecular partition function is as given below:

$$q = q \cdot e^{-E_0/RT}, \quad (2)$$

$E_a$  shows the activation energy, the difference between the zero point energies of transition state complex and reactants [15].

$$k = \frac{k_B T}{h} \cdot \frac{q^\ddagger}{q_A \cdot q_B} \cdot e^{-E_a/RT}, \quad (3)$$

- $k_B$  : Boltzmann constant
- $h$  : Planck constant
- $T$  : absolute temperature

In order to be able to calculate the rate constant, it is necessary to initially calculate the partition function of the activated complex. To realize this calculation, it is essential to know the geometry of the complex and moments of inertia. In addition,  $E_a$  should be known in order to find out the rate constant. The activation energy like the vibration frequency can only be calculated as quantum mechanical.

The most probable reaction path and the yield distribution of the OH radical of every molecule were determined by comparing the obtained results. The optimized geometric structures were drawn via GaussView 5, and the calculations were done via Gaussian 09 packet programme [16].

### *Methodology*

The reaction system under consideration consists of  $\bullet OH$  radicals that are open-shell species. It is well-known that open-shell molecules pose severe problems in quantum mechanical

calculations. Therefore, geometry optimization of the reactants, the product radicals, pre-reactive and transition state complexes were performed with the DFT method with the Gaussian 09 package [16]. DFT methods use the exact electron density to calculate molecular properties and energies, taking electron correlation into account. They do not suffer from spin contamination and this feature makes them suitable for calculations involving open-shell systems. The DFT calculations were carried out by the hybrid B3LYP functional, which combines HF and Becke exchange terms with the Lee–Yang–Parr correlation functional.

Choice of the basis set is very important in such calculations. Based on these results, optimizations in the present study were performed at the B3LYP/6-31G(d) level. The forming C–O bonds in the addition paths and the H–O bond in the abstraction path were chosen as the reaction coordinates in the determination of the transition states. Ground-state and transition-state structures were confirmed by frequency analyses at the same level. Transition structures were characterized by having one imaginary frequency that belonged to the reaction coordinate, corresponding to a first-order saddle point. Zero-point vibrational energies (ZPEs) were calculated at the B3LYP/6-31G(d) level [2].

#### Solvent effect model

In aqueous media, water molecules affect the energetics of the degradation reactions of all organic compounds. Moreover, H<sub>2</sub>O induces geometry relaxation on the solutes. The latter effect becomes more important when hydrogen-bonded complexes are present. However, the results obtained in earlier studies indicate that geometry changes have a negligible effect on the energy of the solute in water for both open- and closed-shell structures [17,18]. In this study, to take into account the effect of H<sub>2</sub>O on the energetics and the kinetics of the aminotoluene + •OH reactions, DFT/B3LYP/6-31+G(d) calculations were carried out for the optimized structures of the reactants, the pre-reactive and the transition state complexes and the product radicals, by using COSMO (conductor-like screening solvation model) [18] as the solvation model, implemented in the Gaussian 09 package. The solvent was water at 25 °C, with dielectric constant  $\epsilon = 78.39$  [19].

COSMO is one of the polarizable continuum methods (PCMs). In PCMs, the solute molecule is placed in a cavity surrounded by a polarizable continuum, whose reaction field modifies the energy and the properties of the solute [20]. The geometry of the cavity is determined by the shape

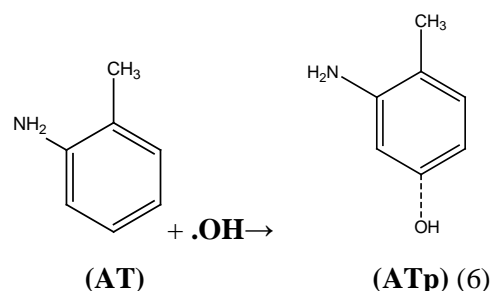
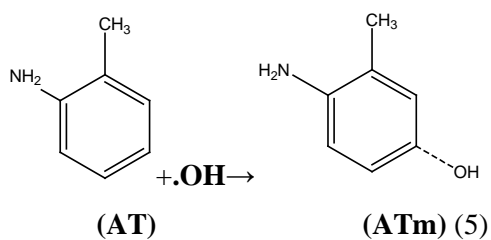
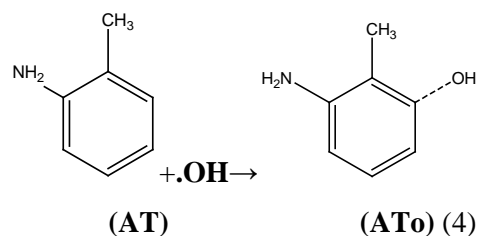
of the solute. The reaction field is described in terms of apparent polarization charges or reaction field factors included in the solute Hamiltonian, so that it is possible to perform iterative procedures leading to self-consistence between the solute wave-function and the solvent polarization. The COSMO method describes the solvent reaction field by means of apparent polarization charges distributed on the cavity surface, which are determined by assuming that the total electrostatic potential cancels out at the surface. This condition can describe the solvation in polar liquids. Hence, it is the method of choice in this study [2].

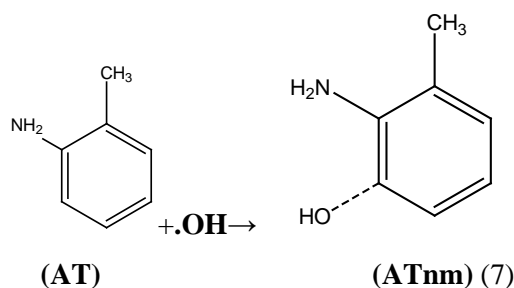
## RESULTS AND DISCUSSION

### Computational modeling

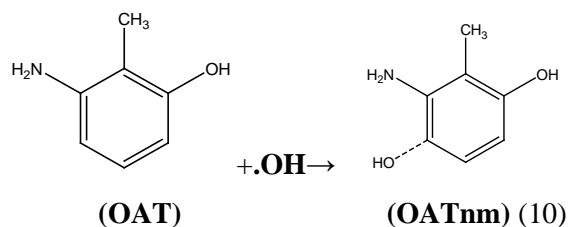
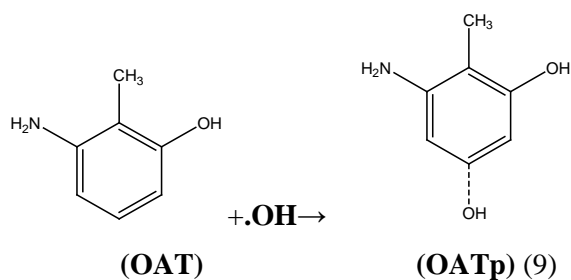
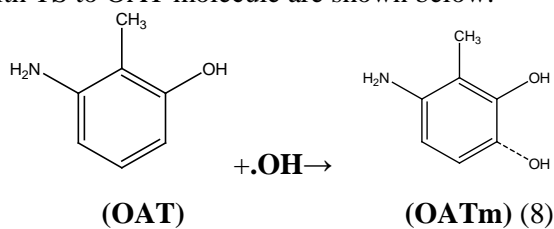
#### Reaction paths

The hydroxyl radical is a very active species and has a strong electrophilic character [21]. Once formed, it can readily attack the aminotoluene molecule and produce the reaction intermediates. •OH radical reactions with aromatic compounds proceed through the following reaction pathway: H-atom abstraction from C–H bonds and addition to aromatic rings [22]. Based on previous results [6,7,8,9,14,23] four different paths for the reaction of aminotoluene(AT) with •OH were determined. The first four paths, o-addition (ATo), m-addition (ATm), p-addition (ATp) and m- addition to NH<sub>2</sub> (ATnm) with TS to AT molecule are shown below:

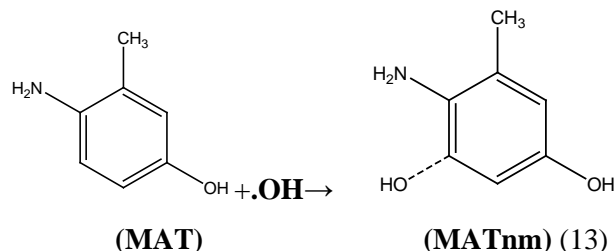
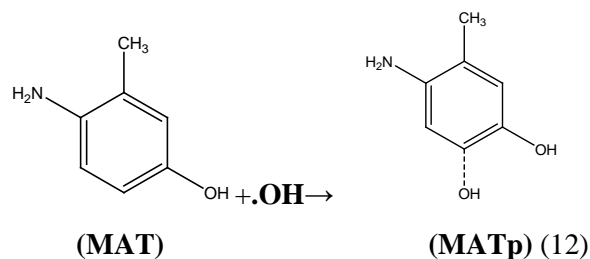
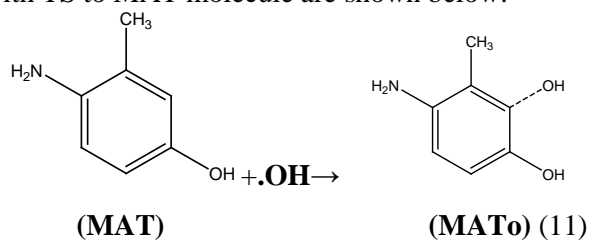




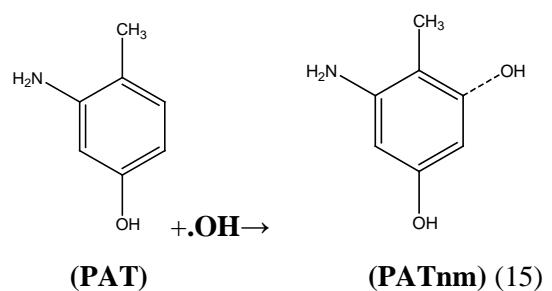
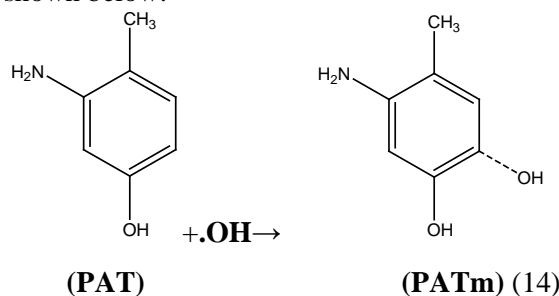
Based on previous results [6,7,8,9,14,23] three different paths for the reaction of 3-hydroxy-2-methyl aniline (OAT) with  $\cdot\text{OH}$  were determined. The first three paths, m-addition (OATm), p-addition (OATp), and m-addition to  $\text{NH}_2$  (OATnm) with TS to OAT molecule are shown below:



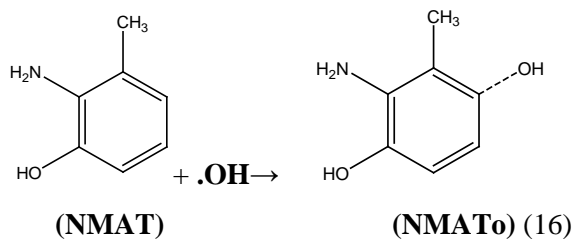
Based on previous results [6,7,8,9,14,23] three different paths for the reaction of 4-hydroxy-2-methyl aniline (MAT) with  $\cdot\text{OH}$  were determined. The first three paths, m-addition (MATo), p-addition (MATp), and m-addition to  $\text{NH}_2$  (MATnm) with TS to MAT molecule are shown below:

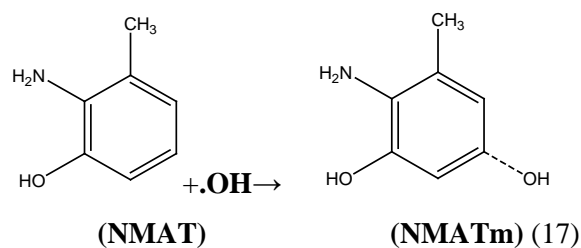


Based on previous results [6,7,8,9,14,23] two different paths for the reaction of 5-hydroxy-2-methyl aniline (PAT) with  $\cdot\text{OH}$  were determined. The first two paths, m-addition (PATm) and m-addition to  $\text{NH}_2$  (PATnm) with TS to PAT molecule are shown below:



Based on previous results [6,7,8,9,14,23] two different paths for the reaction of 2-hydroxy-6-methyl aniline (NMAT) with  $\cdot\text{OH}$  were determined. The first two paths, o-addition (NMATo) and m-addition (NMATm) with TS to NMAT molecule are shown below:





#### Transition State Complexes

In this study, reactants were used to find out the transition state complexes. An estimation of the initial geometry was done according to the type of reaction path using the optimum geometric parameters of reactants. C-O bond was chosen as the reaction coordinate while modeling the transition state complexes for the reactions realized with OH addition, and the bond length was changed as 1.850-2.500 Å during calculation. The emerging OH bond length was chosen as the reaction path, and in order to determine the position of the OH radical according to the molecule, the dihedral angles belonging to this group were changed during calculations. Activation energies and their most determined state in thermodynamic terms for gas phase and aqueous media were calculated for the probable reaction paths of all transition state complexes.

According to Fig.1, the C-O bond lengths at four probable transition states of the OH radical were taken as precise measurement. The bond lengths were calculated as ATo (2.76 Å), ATm (3.44 Å), ATp (2.03 Å), ATnm (3.63 Å) relatively. The longest C-O bond belongs to ATnm TS molecule and it is found out that it occurs later compared to the others. Therefore, it is the most probable transition state.

According to Fig.2, the C-O bond lengths at three probable transition states of the OH radical were measured. The bond lengths were calculated as OATm (2.06 Å), OATp (2.03 Å), OATnm (2.70 Å), MATo (2.09 Å), MATp (2.11 Å), MATnm (2.64 Å), respectively. The longest C-O bonds belong to OATnm and MATnm TS molecules and they are found to occur later than the others. Therefore, they are the most probable transition states.

According to Fig.3, the C-O bond lengths at four probable transition states of the OH radical were measured. The bond lengths were calculated as PATm (2,05 Å), PATnm (2,91 Å), NMATo (2,06 Å), NMATm (2,14 Å), respectively. The longest C-

O bonds belong to ATnm and NMATm TS molecules and they are found to occur later than the others. Therefore, they are the most probable transition states.

#### CONCLUSIONS

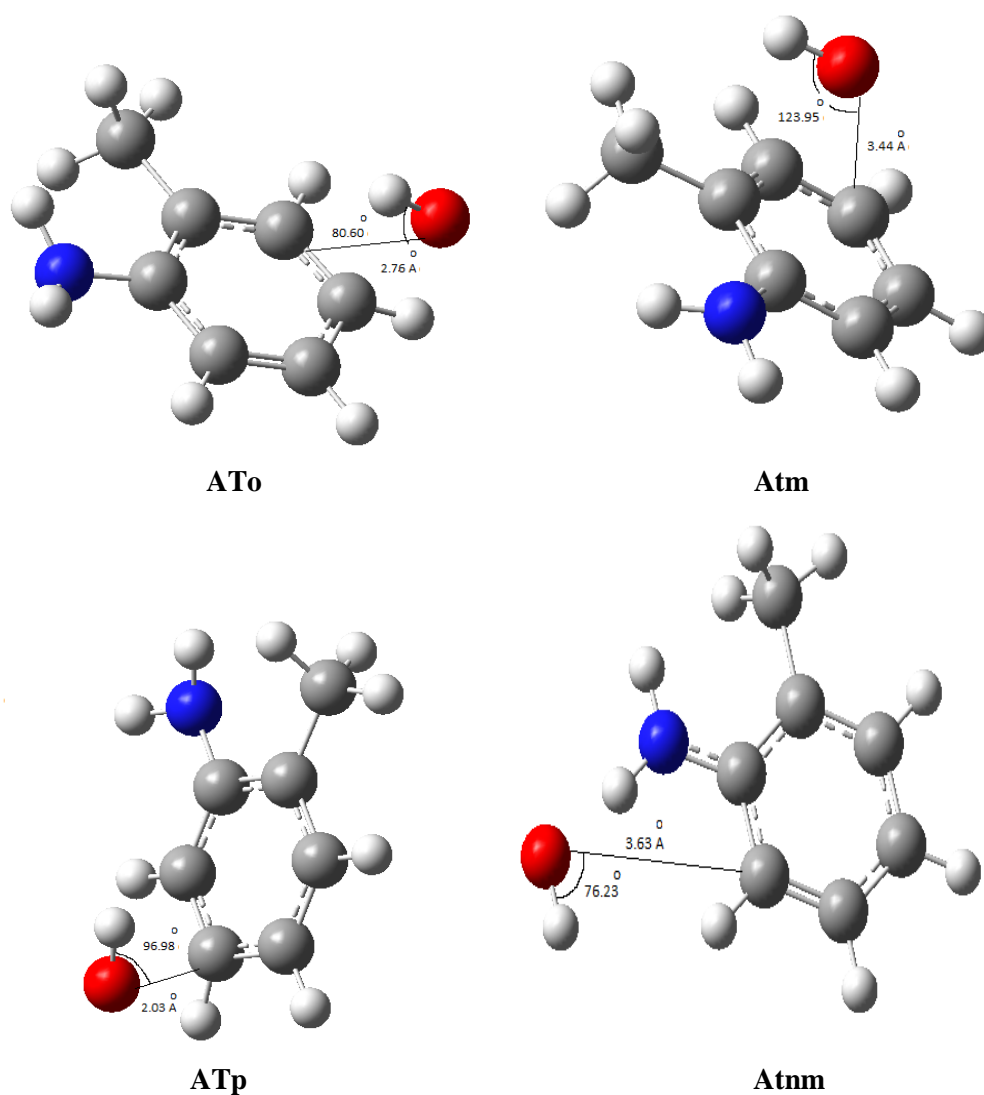
Organic contaminants exist at very low concentrations in water [3]. Therefore, it is essential to remove the organic contaminants from drinking water [4]. Hydroxyl radical which is the most reactive type known in biological systems reacts with every biomolecule it encounters including water. Potentially, every biomolecule is a hydroxyl radical scavenger at a different speed [8]. Aromatic compounds are good detectors since they hydroxylate. In addition, the position of attack to the ring depends on the electron withdrawal and repulsion of previously present substituents [9]. When the Mulliken loads in Table 2 are analysed, the electronegativities of N and O atoms give us information about the bonding state of the OH radical.

In Table 1, the activation energy levels of  $E_a$  gas phase of the TS molecules having the lowest energy at DFT method for every transition state complex are given below:

-7,404 kcal/mol of ATnm for AT,  $-1.321 \times 10^1$  kcal/mol of OATm for OAT,  $-5.131$  kcal/mol of MATnm for MAT,  $-1,293 \times 10^1$  kcal/mol of PATm for PAT and  $-6.359$  kcal/mol of NMATm for NMAT are the transition state complexes with the lowest energy. These reveal the most probable transition state complexes in the gas phase. The most rapid occurring transition state complex in the gas phase have the highest values of the  $k$  rate constant.

$E_{a_{\text{ecosmo}}}$  aqueous media activation energy levels at DFT method are  $0.623 \times 10^1$  kcal/mol of ATp for AT,  $0.183 \times 10^1$  kcal/mol of OATm for OAT,  $0.673 \times 10^1$  kcal/mol of ATnm for MAT,  $0.763 \times 10^1$  kcal/mol of PATnm for PAT,  $0.210 \times 10^1$  kcal/mol of NMATo for NMAT are the transition state complexes with the lowest energy. This reveals that it is the most probable transition state at aqueous media.

Hydroxyl radicals are used in order to remove organic contaminants from water. In this study, the most probable reaction paths, where OH radical is added to the aromatic ring, were determined.



**Fig. 1.** Optimized structures of the transition state complexes of probable reaction paths (4,5,6,7).

**Table 1.** k and energy levels calculated via DFT method

DFT	Ea(kcal/mol)	k	Ea <sub>ecosmo</sub> (kcal/mol)
ATo	-5.964	$1.145 \times 10^{11}$	$5.307 \times 10^1$
ATm	-1.797	$3.738 \times 10^8$	$2.111 \times 10^1$
ATp	-3.480	$1.568 \times 10^9$	<b><math>0.623 \times 10^1</math></b>
ATnm	<b>-7.404</b>	<b><math>2.257 \times 10^{12}</math></b>	$1.927 \times 10^1$
OATm	<b><math>-1.321 \times 10^1</math></b>	<b><math>6.028 \times 10^{15}</math></b>	<b><math>0.183 \times 10^1</math></b>
OATp	-3.275	$1.376 \times 10^9$	$1.211 \times 10^1$
OATnm	-3.077	$1.005 \times 10^9$	$1.856 \times 10^2$
MATo	-4.953	<b><math>2.386 \times 10^{10}</math></b>	$1.647 \times 10^1$
MATp	-4.976	$1.905 \times 10^{10}$	$1.324 \times 10^2$
MATnm	<b>-5.131</b>	$9.504 \times 10^4$	<b><math>0.673 \times 10^1</math></b>
PATm	<b><math>-1.293 \times 10^1</math></b>	<b><math>4.015 \times 10^{15}</math></b>	$0.767 \times 10^1$
PATnm	-4.049	$1.139 \times 10^{10}$	<b><math>0.763 \times 10^1</math></b>
NMATo	-5.402	$5.070 \times 10^{10}$	<b><math>0.210 \times 10^1</math></b>
NMATm	<b>-6.359</b>	<b><math>2.505 \times 10^{11}</math></b>	$0.607 \times 10^1$

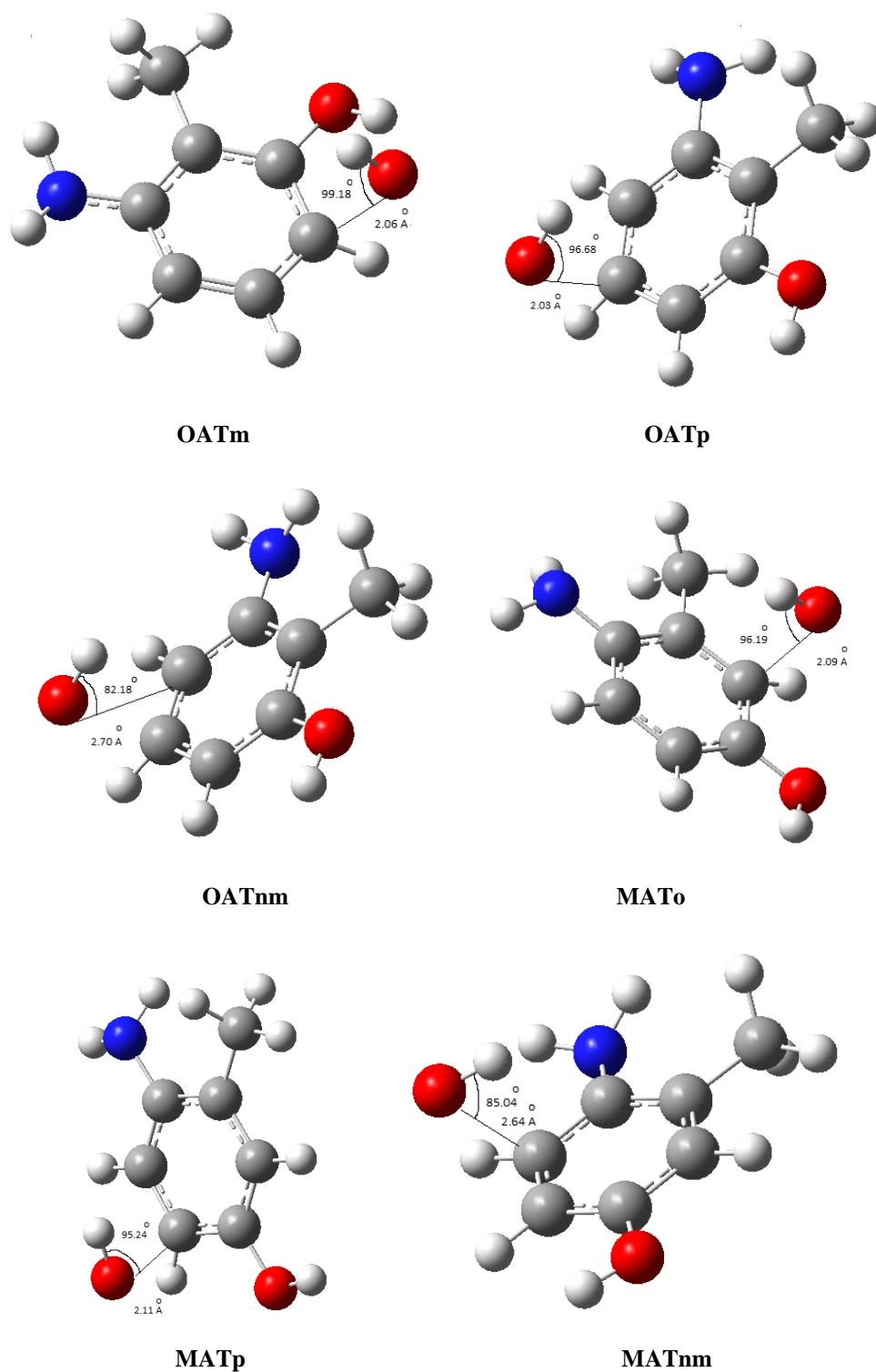


Fig. 2. Optimized structures of the transition state complexes of probable reaction paths (8, 9, 10).

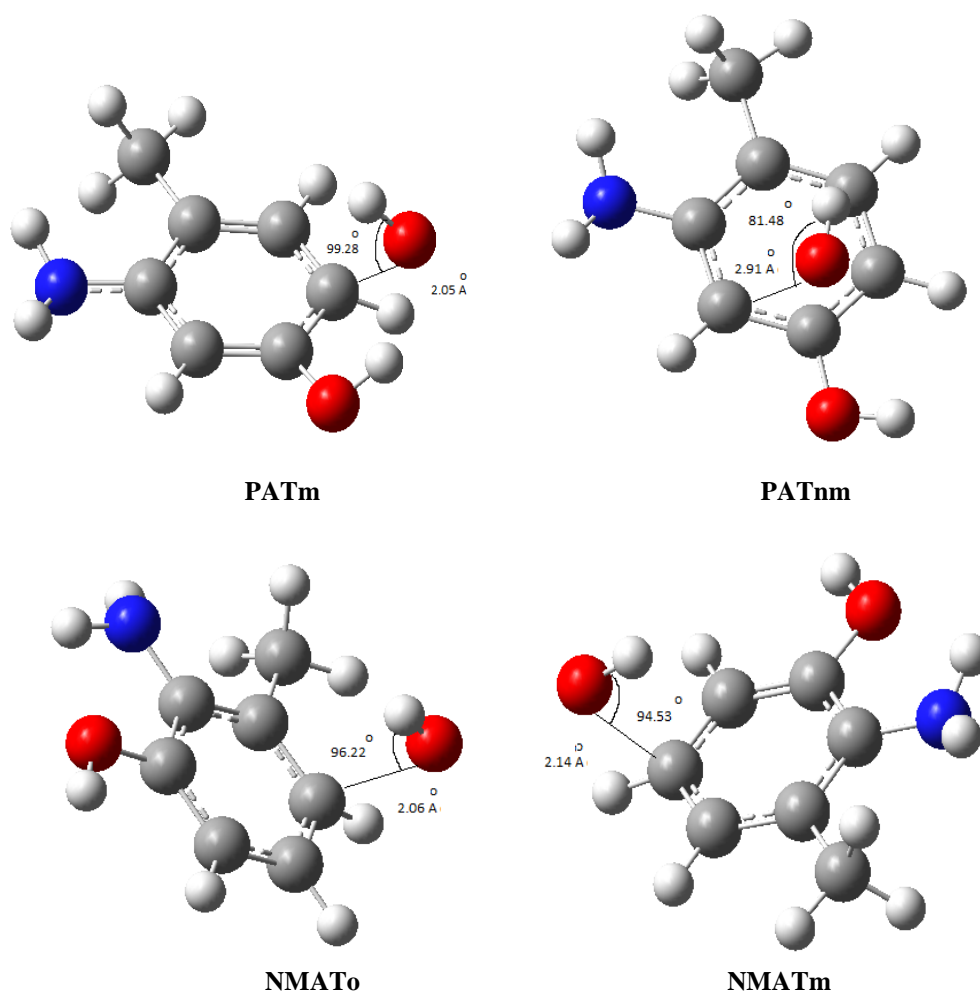


Fig. 3. Optimized structures of the transition state complexes of probable reaction paths (11, 12, 13, 14).

Table 2. Mulliken loads of the heavy atoms of the studied molecules

AT		ATo		ATm		ATp	
11 C	-0.079158	11 C	-0.068813	11 C	-0.084916	11 C	-0.060090
15 N	-0.152651	15 N	-0.128493	15 N	-0.145308	15 N	-0.145132
		18 O	-0.219771	18 O	-0.114680	18 O	-0.209659
ATnm		OAT		OATm		OATp	
11 C	-0.063830	10 C	-0.062126	10 C	-0.055300	10 C	-0.040231
15 N	-0.068889	14 N	-0.151131	14 N	-0.118889	14 N	-0.144576
18 O	-0.231787	17 O	-0.246327	17 O	-0.226425	17 O	-0.240401
				19 O	-0.285348	19 O	-0.204711
OAT nm		MAT		MATo		MATp	
10 C	-0.041225	10 O	-0.253210	10 O	-0.216734	10 O	-0.216065
14 N	-0.145082	12 N	-0.160178	12 N	-0.151373	12 N	-0.149771
17 O	-0.240589	15 C	-0.074152	15 C	-0.049042	15 C	-0.057486
19 O	-0.211082			19 O	-0.202878	19 O	-0.206673
MATnm		PAT		PATo		PATm	
10 O	-0.243592	10 C	-0.086504	10 C	-0.005234	10 C	-0.067938
12 N	-0.150491	14 N	-0.152124	14 N	-0.221558	14 N	-0.119865
15 C	-0.063696	17 O	-0.245155	17 O	-0.252320	17 O	-0.224289
19 O	-0.097024			19 O	-0.095696	19 O	-0.285990
PATnm		NMAT		NMATo		NMATm	
10 C	-0.074263	10 C	-0.076104	10 C	-0.050241	10 C	-0.066739
14 N	-0.144674	14 O	-0.262806	14 O	-0.239830	14 O	-0.256092
17 O	-0.229721	16 N	-0.141021	16 N	-0.133101	16 N	-0.114022
19 O	-0.097927			19 O	-0.220675	19 O	-0.223159



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## АНАЛИЗ НА РЕАКЦИОННАТА КИНЕТИКА НА МОЛЕКУЛАТА НА АМИНОТОЛУЕН ЧРЕЗ DFT-МЕТОДА

Б. Ерен, И. Ялчин Гуркан \*

*Департамент по химия, Университет „Намик Кемал“, Текирдаг, Турция*

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(Резюме)

В тази работа се анализират най-вероятните маршрути на реакцията на аминотолуен (о-толуидин) с ОН-радикали. Оптимизираната геометрия е изчислена чрез софтуера Gauss View 5. Най-ниските енергийни нива са намерени чрез геометрична оптимизация с програмата Gaussian 09. Изчислени са и геометричната структура и дължината на връзките. Тази работа има за цел да се определят най-вероятните пътища на продуктите от взаимодействието между аминотолуена и ОН-радикалите в газова и в течна фаза. Използвани са квантово-механични методи за посочване на влиянието на скоростта на реакцията върху първичните преходни съединения, хидроксилираните междинни съединения и на водата като разтворител.

Междинните съединения, геометричната оптимизация на реагентите и преходните комплекси са определени по DFT-метода. На базата на квантово-механични пресмятания с използването на теорията на преходните състояния (TST) са определени всички вероятни скоростни константи. Връзките C-O са взети като референтни при определянето на преходните състояния. Активиращата енергия за вероятните реакционни маршрути за всички преходни комплекси и техните най-устойчиви състояния са изчислени от термодинамична гледна точка за газовата и течната фаза. Въздействието на разтворителя (вода) е изследвано чрез COSMO-софтуер като солватационен модел.