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Modeling of condensation reaction of aniline to diphenylamine by PM7 method

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Abstract

Modeling of the condensation reaction to diphenylamine was carried out by PM7 method with acid catalysts: tetrafluoroborate, oxytrifluoroborate and anilinium oxytetrafluoroborate. The calculated data prove that the formation of a few protonated forms of aniline is possible during the reaction of aniline with acids. Only positively charged *p*- and *o*- σ -complexes are capable of further interaction with aniline. The stage of intramolecular proton transfer from the primary to the secondary amino groups of intermediates of aniline reaction with proton aniline σ -complex determines the condensation rate of aniline to diphenylamine with acid catalysts. A catalyst anion can form ionic and ion-dipole complexes with reaction mixture components and can influence the distribution of electron density in reactants and their reactivity with its field.

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1. Introduction

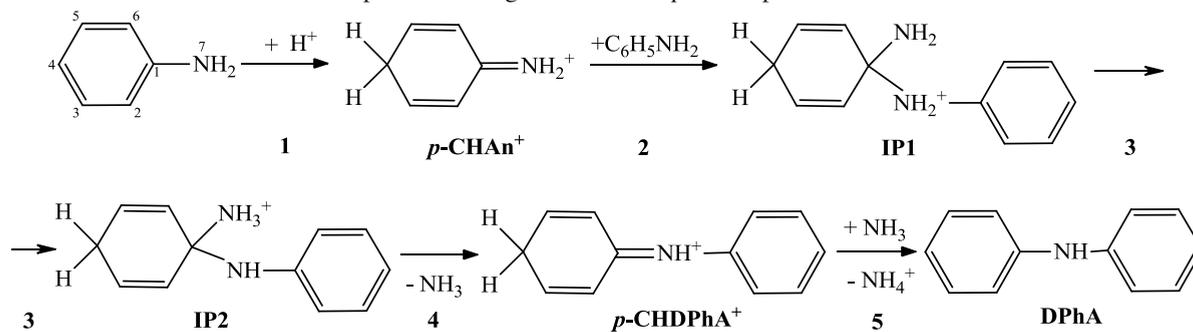
Currently, condensation reaction of aniline catalyzed by acid is the main method for industrial production of diphenylamine (DPhA)¹. The most widely catalysts used are mineral acids, silica-alumina catalysts, catalysts containing both fluorine and boron, fluorine and phosphorus, alumina modified by hydrochloric, boric, phosphoric acids and boron trifluoride². There are a numerous amount of patents of DPhA obtaining from aniline. Unfortunately, the scientific literature has almost no information about the mechanism of the processes and the role of acid catalysts in a reaction of aromatic nucleophilic substitution.

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Seeboth H.³, Basu J. K. and colleagues⁴ have supposed that active OH groups are proton carriers at the surface of a heterogeneous catalyst (γ -Al₂O₃, activated by mineral acids and/or boron trifluoride). Interaction of surface OH-groups of catalysts with the amino group of aniline leads to the ammonium ion formation. In this case, C-N-bond becomes weaker, releasing the ammonia molecule with formation of a phenyl cation and catalyst anion.

The ion of diphenyl ammonia is formed due to nucleophilic reaction of phenyl cation with aniline. Then it is converted to DPhA giving a proton to the catalyst anion. This mechanism involves strong participation of catalyst for loosen of C-N-bond, as energy of C-N-bond breakage for anilinium cation is very high ($E_{C-N} = 377$ kJ/mol). Upon the research of literary and experimental data, the authors of the article² have supposed that the reaction of aniline condensation to DPhA can proceed through formation of *p*- σ -complex intermediate.



Scheme 1. Mechanism of condensation reaction of aniline to DPhA

A proton can be transferred by aniline, catalyst or a solvent molecule. The energy barriers of the stages specifying the reaction rate may change depending on the nature of the substance that transfer a proton. Numerous experimental data indicate that the nature of the acid catalyst has a significant effect on the rate and selectivity of the condensation process.

Catalysts containing boron trifluoride are widely used in industrial production. These catalysts are used in liquid-phase processes, e.g. ammonium oxotetrafluoroborate (NH₄)₂O(BF₃)₄⁵, anilinium oxytrifluoroborate C₆H₅NH₃[HOBF₃]⁶, fluoroborates of variable composition^{7,8}. They are also used in gas-phase processes, e.g. the modified zeolites by boron trifluoride⁹.

Quantum-chemical methods of modeling are often used to study and optimize the technology of modern chemical processes.¹⁰ This study presents modeling of the condensation reaction of aniline to DPhA with boron trifluoride, anilinium oxytrifluoroborate, anilinium oxotetrafluoroborate to reveal controlling step of the process and influence of the catalyst on the condensation process by PM7 method.

2. Computational Methods

Quantum-chemical calculations were carried out using the following software: ChemBio3D Ultra V. 12.0.2.1076¹¹ and MOPAC2012¹². Geometrical parameters (i.e. bond length, angles of valence and torsion angles) that determine the position of atoms in relation to one another and to the reaction center were improved according to the standard procedure. The optimization of geometrical parameters of transition states was carried out according to the standard TS-procedure¹².

We performed experimental calculations using various methods with the following software: MOPAC2012 and ChemBio3D Ultra to choose a method of calculation.

We used DPhA as a test compound. The calculated values of thermodynamic functions are in Table 1.

Table 1. Calculated and experimental thermodynamic data of DPhA

Thermodynamic functions	MNDO	PM6	PM7	HF 3-21G	DFT B3LYP 3-21G	Experimental data ¹³
S ^o ₂₉₈ (g), J/(mol·K)	432.64	434.56	430.84	407.73	415.61	407.94

$\Delta H_f^{\circ}{}_{298}$ (g), kJ/mol	232.60	205.79	210.43	589.90	554.50	201.67
$\Delta G_f^{\circ}{}_{298}$ (g), kJ/mol	366.60	340.61	344.97	468.33	430.58	343.09

As it can be seen from the data given, the least discrepancy between experimental and calculated data is for PM6 and PM7 methods. The ab initio methods HF 3-21G and DFT B3LYP/3-21G shows the biggest deviations of the calculated values from experimental data and, thus, cannot be used for modeling of the reaction for DPhA formation. Considering the above and the recommendations of MOPAC2012 developers¹², we used a semi empirical PM7 method for further calculations.

3. Results and discussion

The location of aniline protonation in the gas phase is a contentious issue during last 30 years. At the same time, the above question was repeatedly investigated by both calculated and experimental methods. Theoretical methods of G2MP2 and B3LYP calculation show that the proton affinity to the carbon atom in p-position of the aromatic ring and the nitrogen atom of aniline are comparable¹⁶.

In the presence of acid catalysts the formation of the protonated form of aniline occurs. The calculation results of different aniline protonated forms by PM7 method are shown in Fig. 1.

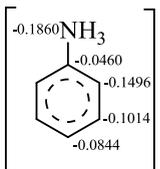
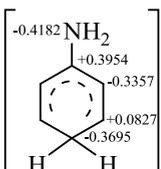
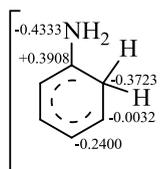
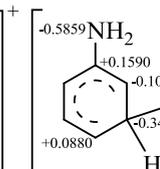
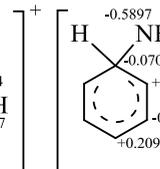
					
	NHAn⁺	p-CHAn⁺	o-CHAn⁺	m-CHAn⁺	ipso-CHAn⁺
$S^{\circ}{}_{298}$, J/(mol·K)	333.21	317.90	323.34	333.34	315.51
$\Delta H_f^{\circ}{}_{298}$, kJ/mol	746.03	755.35	766.63	868.70	944.26
$\Delta G_f^{\circ}{}_{298}$, kJ/mol	841.10	854.99	864.65	963.73	1044.61

Fig. 1. The calculated values of atom charges and enthalpy of formation different protonated forms of aniline

As it can be seen from the data given, the stability of the protonated forms of aniline is presented in the following order: **NHAn⁺** \approx **p-CHAn⁺** \approx **o-CHAn⁺** \gg **m-CHAn⁺** \gg **ipso-CHAn⁺**.

These results are in good agreement with the ones of the research¹⁶ and confirm the conclusions of the research². First of all, attack of nucleophile (aniline) on its protonated form will occur at the concentration area of the greatest positive charge, i.e. C1 atom. The attack on the carbon atoms C2, C3 and C4 is less probable.

Therefore, only **p-CHAn⁺** and **o-CHAn⁺** are considered to be an object of nucleophilic attack of aniline on the carbon atom ring.

In accordance with the purpose the modeling of the following reactions was carried out:



Energy diagram of the profile of the aniline reaction way with **p-CHAn⁺** and **o-CHAn⁺** is represented in Fig. 2 according to the reaction scheme.

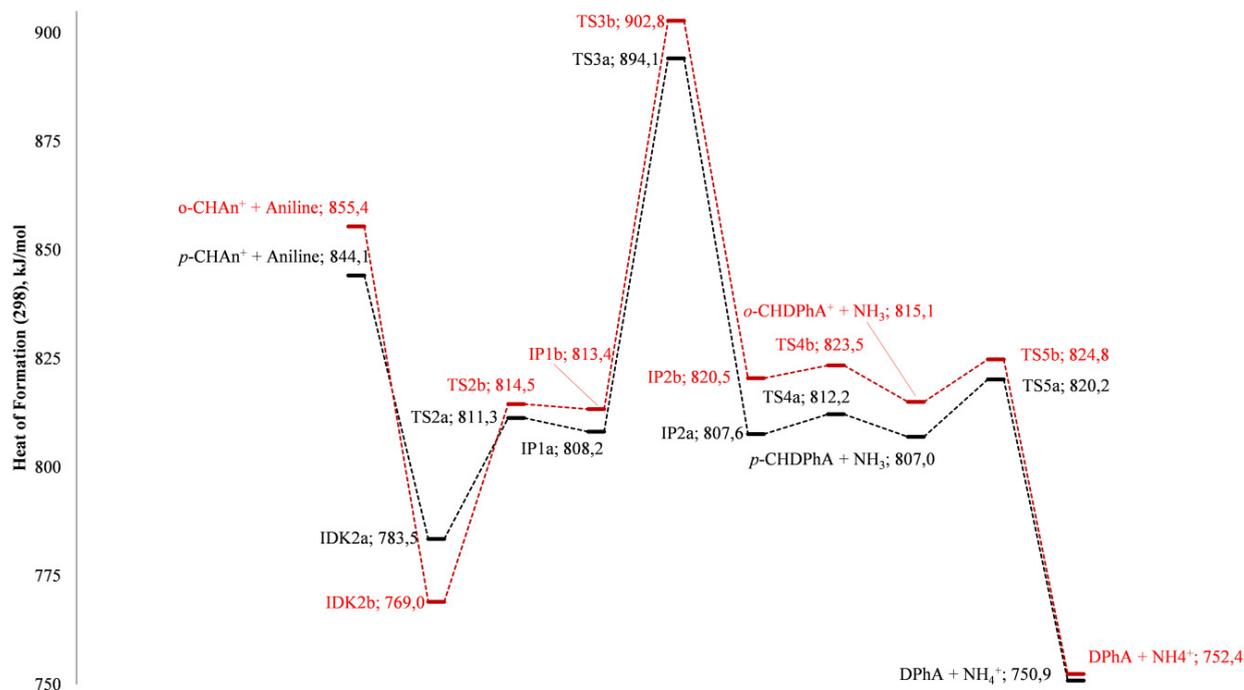


Fig. 2. Computed reaction profile for the reaction of $C_6H_5NH_2$ and $p\text{-CHAN}^+$ (a, black line) and $p\text{-CHAN}^+$ (b, red line).

The product formation of the **IP1** adjoining occurs through the intermediate **IDK2** complex, which is formed by ion-dipole interaction of $p\text{-CHAN}^+$ ($o\text{-CHAN}^+$) with the nucleophilic center of aniline. The energy barrier of ion-dipole **IDK** complex transition in **IP1** is 27.85 kJ/mol (reaction a) and 45.51 kJ/mol (reaction b).

In **IP1a** compared with $p\text{-CHAN}^+$ the bond orders of $C^1\text{-N}^7$ (1.0651) $C^1\text{-C}^2$ (1.0112) and $C^3\text{-C}^4$ (1.0253) decrease on -0.4363, -0.1043 and -0.0211 points, respectively. Also, bond orders of $C^2\text{-C}^3$ (1.9087) and $C^5\text{-C}^6$ (1.8959) increase on the 0.1152 and the 0.1278 points, respectively. The order of $C^1\text{-N}^{21}$ bond formation is 0.6896. This indicates that **IP1a** has a diene ring structure, C1 and C4 atoms have sp^3 -hybridization.

A similar situation is observed on **IP1b** in comparison with $o\text{-CHAN}^+$. The bond orders of $C^1\text{-N}^7$ (1.0770), $C^1\text{-C}^2$ (0.9903), $C^2\text{-C}^3$ (1.0163), $C^4\text{-C}^5$ (1.0819), $C^1\text{-C}^6$ (1.0129) decrease on -0.4199, -0.0400, -0.0093, 0.0602 and -0.1738 points, respectively. The bond orders of $C^3\text{-C}^4$ (1.8829) and $C^5\text{-C}^6$ (1.8429) increase on 0.0684 and 0.1999 points, respectively. The order of **IP1b** bond formation of $C^1\text{-N}^{21}$ is 0.6862. The diene ring structure is implemented in **IP1b**, C1 and C2 atoms have sp^3 -hybridization.

Further transformation of the unstable addition **IP1** product can occur in two ways. In the first case, the proton transfer is carried out by one hydrogen atom abstraction in the sp^3 -hybridized C atom and addition it to the primary amino group. The calculations of the reaction route showed that deprotonation leads to destabilization of the addition product, and it decomposed up to initial reagents.

In the second case, stabilization is possible by proton transfer from the secondary to the primary amino group with basicity of a larger degree (stage 3, **IP1** \rightarrow **IP2**). Two possible reaction routes were considered during proton transfer in the addition product. In the first way, deprotonation is carried out by the internal vibrational energy of N-H bond and occurs intramolecularly (activation energy - 85.93 kJ/mol for **IP1a** \rightarrow **IP2a**; 89.42 kJ/mol for **IP1b** \rightarrow **IP2b**). In the second way, proton transfer occurs under the action of the ammonia molecule that attacks the reaction center (activation energy - 149.8 kJ/mol for **IP1a** \rightarrow **IP2a**). These results suggest that the intramolecular proton transfer is more preferable to the intermolecular proton transfer involving ammonia (or solvent). It should be noted that stage 3 has the highest activation energy and is a rate-determined stage of the condensation process.

The positive charge in IP2 is focused on the primary amino group. The C¹-N⁷ bond order (0.6871 for **IP2a**, 0.7036 for **IP2b**) is small, which makes easier break the ammonia molecule from this intermediate compound (stage 4). The energy barrier of formation reaction of the σ -complexes of *p*-CHDPhA⁺ and *o*-CHDPhA⁺ is - 4.56 and - 2.94 kJ/mol, respectively.

The deprotonation of the CHDPhA⁺ σ -complex (stage 5) takes place by action of the ammonia molecule departing. The energy barrier transition from CHDPhA⁺ into final products of DPhA and NH₄⁺ is - 13.21 kJ/mol for *p*-CHDPhA⁺ and is 9.78 kJ/mol for *o*-CHDPhA⁺.

The results of the calculations show that the stage of the intramolecular proton transfer from the secondary to the primary amino groups in the intermediate of aniline and aniline σ -complex interreaction with a proton is a rate-determining step of the process.

Modelling of reactions (a), (b), (c) shows that the nature of the catalyst significantly affect the interaction energy of the reactants at all stages of the condensation process. When using different catalysts (H[BF₄], H[HO(BF₃)], H₂[O(BF₃)₄]) the activation energy of the rate determining stage 3 is 60.38, 60.21 and 91.24 kJ/mol, respectively. The results are in good agreement with the experimental data ($E_{act} = 69.5$ kJ/mol) of the liquid-phase process of DPhA obtaining in the presence of aniline salt of oxytrifluoroborate acid¹⁷.

The calculations indicate that the anion of the catalyst can form ionic and ion-dipole complexes with the components of the reaction mixture. Also, the anion of the catalyst affects the electron density distribution in the reactants (their reactivity). The activity of the catalyst is determined by its charge and geometric sizes. The geometrical structures of transition states of **TS3a**, **TS3b**, **TS3c**, **TS3d**, **TS3e** are shown in Fig. 3.

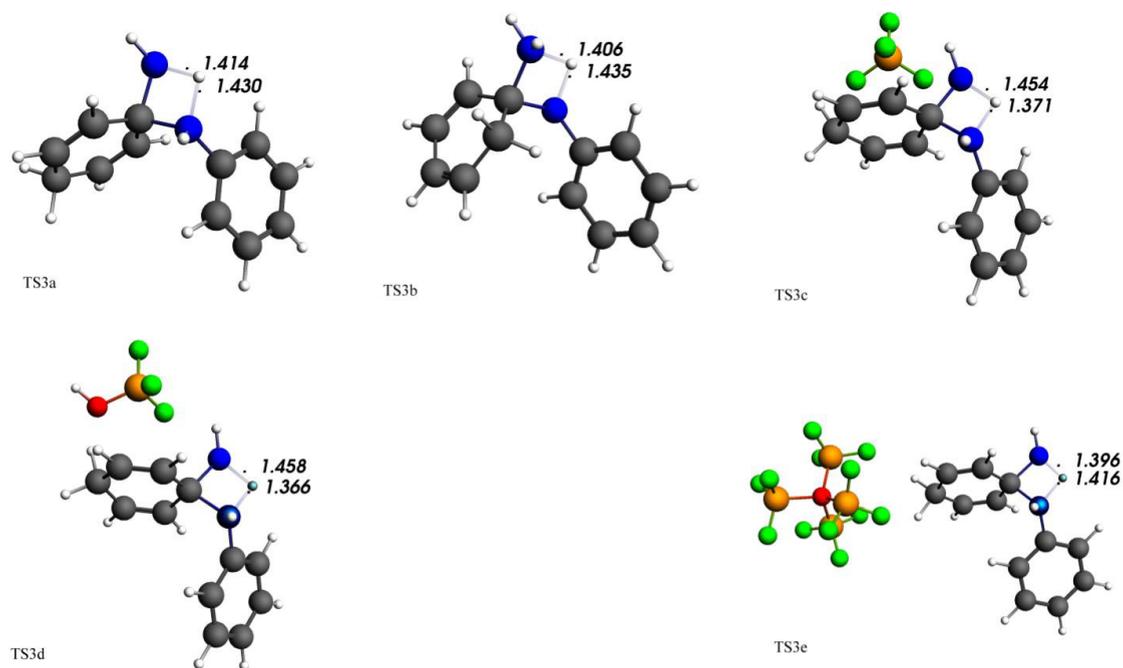


Fig. 3. The structures of the transition states of TS3a, TS3b, TS3c, TS3d, TS3e.

Definitely, geometry of the TS3c and TS3d transition states indicates a strong ionic interaction of $[\text{BF}_4]^-$ and $[\text{HO}(\text{BF}_3)]^-$ anions with the aromatic ring of the positively charged σ -complex and the absence of such interaction for $[\text{O}(\text{BF}_3)_4]^{2-}$ anion.

4. Summary

The stage of intramolecular proton transfer from the primary to the secondary amino groups of the intermediates of aniline reaction with proton aniline σ -complex determines the rate of condensation of aniline to diphenylamine with acid catalysts.

A catalyst anion activates initial reagents, intermediates and stabilizes the final products. This mechanism is the following: the catalyst anion can form ionic and ion-dipole complexes with the reaction mixture components and can influence the distribution of electron density in reactants and their reactivity. Thus, the results of this research can be used for selection of liquid or gas phase catalysts of the process.

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