REACTIONS OF DIPHENYLAMINE WITH BENZENEDIAZONIA: A QUANTUM CHEMICAL TREATMENT INVOLVING EXPLICIT AQUEOUS MEDIUM ACCOUNT

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Aqueous medium has been established to exert a considerable influence upon the reaction rate for 4-carboxybenzenediazonium, 4-nitrobenzenediazonium and 4-sulphobenzenediazonium cations with diphenylamine. Furthermore, this medium stabilizes predominantly the σ-complex occurring on electrophilic attack by 4-sulphobenzenediazonium of *para* position in the diphenylamine molecule, and in doing so it chooses between two alternative routes of azo coupling reaction, which are predicted by the quantum chemical computations of isolated σ-adducts.

INTRODUCTION

The work[1] reports on the study, using the electron absorption spectroscopy, of the azo coupling reaction of diphenylamine (DPA) with the 4-carboxybenzenediazonium (**I**), 4-nitrobenzenediazonium (**II**) and 4-sulphobenzenediazonium (**III**) cations in aqueous medium and in micelles of anionic surfactant, sodium dodecylsulphate. It has been established[1] that the rate of azo coupling reaction in aqueous solutions follows the sequence **II** > **III** $\gtrless$ **I**, and in the micellar medium **II** > **I** > **III**. For **I**, **II**, and **III**, the rate constants are 35, 80, and 38 $l^2 \cdot mol^{-2} \cdot min^{-2}$, respectively, in the aqueous medium, and 85, 270, and 7.2 $l^2 \cdot mol^{-2} \cdot min^{-2}$, respectively, in the presence of micelles.[1]

The cation **III** is a diazo component of the analytical Griess reaction.[2, 3] The purpose of the present work consists in a quantum chemical study of the regioselectivity of DPA coupling with the above cation, as well as in a comparative analysis of the reactivity over the series of diazonium cations **I-III**.

COMPUTATIONAL METHODS

The computations were performed by means of the PM3 method[4] using the software from the *MOPAC* package[5,6] with the complete geometry optimization (Broyden - Fletcher - Goldfarb - Shanno function minimizer[7] involving Thiel's fast minimization algorithm.[8] The preliminary optimization was realized by the molecular mechanics method (the MMX procedure)[9] with the software of the *PCMODEL* complex.[9] In quantum chemical computations, the condition of the gradient norm not exceeding 0.02 kcal/(mol·Å) was preset. In some cases, the sufficient decrease in gradient norm was achieved by means of abandonment of the Thiel's fast minimization routine (the keyword NOTHIEL of the *MOPAC* package was applied), or under optimization with the Davidon - Fletcher - Powell method (keyword DFP),[7] or using combined approaches involving the keywords NOTHIEL and DFP.

For computing clusters with 157 water molecules included, the PM3 method was used, within the *HyperChem* package [HyperChem (TM),

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Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, U. S. A.]. Complete geometry optimization was carried out by means of the Polak - Ribiere conjugate gradient algorithm.[7] A minimal distance of 1.7 Å was assumed between the solute and water molecules.

The lg$P$ calculations were performed by means of *HyperChem* within an additivity scheme using atomic and bond parameters.[10-13]

RESULTS AND DISCUSSION

In the chapter[14] of the monograph *Quantum Chemistry Research Trends*, we have substantiated the use of quantum chemical methods (*ab initio*, DFT, and semiempirical) of different hierarchy and theory level, adequate to the problems to be solved. In order to the theoretical evaluation of thermodynamic characteristics of "classical" organic compounds and reactions with their participation could be sufficiently simplified, it seems reasonable to appeal to the high-parameterized semiempirical quantum chemical methods.

By means of the PM3 method we computed (Table 1) the standard heats of formations (ΔH_f), entropies (S), free energies of formation (ΔG_f) of DPA, cations **I-III** and azo coupling intermediates - cationic Wheland *trans*-σ-complexes.[15-17]

The standard free energy ΔG_f values were calculated from the relationship:

$$\Delta G_f = \Delta H_f - T\Delta S_f,$$

where the standard entropies of formation ΔS_f were calculated by the formula:

$$\Delta S_f = S - \sum_i S_i ,$$

in which S_i are the entropies of the elements constituting molecule in their standard states[18] in view of

hydrogen, oxygen, sulphur being the two-atomic molecules; T = 298.15 K.

The contributions of separate degrees of freedom for translation, rotation and vibration motions to entropy were computed in the rigid molecule approximation (barriers of rotation and inversion far exceed kT) with no allowance for vibrations anharmonicity. The translation contributions were calculated without using quantum chemical computations, and the rotation contributions relying on the data on equilibrium internuclear distances obtained in the course of quantum chemical treatment. Finally, the contributions of vibration components of entropy were evaluated on the basis of normal vibrations frequencies computed by the quantum chemical method. For computing the frequencies after geometry optimization, second-order derivatives of total energy by natural coordinates (force constants) were preliminary computed.[19]

In calculating the rotational contributions to thermodynamic functions the symmetry number was taken as unity.

Correctness of the computations performed is sustained by reproduction of the experimental[18] standard values of gaseous-phase thermodynamic quantities of DPA (Table 1). According to,[18] for diphenylamine, ΔH_f = 48.20 kcal/mol, S = 97.5 cal/(mol·K), and ΔG_f = 82.00 kcal/mol.

On simulating the barriers of azo coupling reactions in the localization approximation[15, 17, 20-22] we computed the enthalpies ($\Delta\Delta H_f$) and free energies ($\Delta\Delta G_f$) of cationic localization (Table 2):

$$\Delta\Delta H_f = \Delta H_f(\text{DPA}) + \Delta H_f(\text{R-N}^+\equiv\text{N}) - \Delta H_f(\sigma\text{-complex}),$$

$$\Delta\Delta G_f = \Delta G_f(\text{DPA}) + \Delta G_f(\text{R-N}^+\equiv\text{N}) - \Delta G_f(\sigma\text{-complex}),$$

where R-N$^+\equiv$N is benzenediazonium **I**, **II**, or **III**.

Table 1

Computed ΔH_f, S, ΔG_f values

Compound	ΔH_f, kcal/mol	S, cal/(mol·K)	ΔG_f, kcal/mol
DPA	51.27	102.11	83.70
I	164.04	96.84	189.52
II	253.68	91.94	282.39
III	137.34	107.40	167.71
para-σ-Complex of the reaction DPA + **I**	199.26	156.88	269.71
para-σ-Complex of the reaction DPA + **II**	283.62	155.11	356.37
ortho-σ-Complex (**IV**) of the reaction DPA + **III**	171.54	167.81	246.78
meta-σ-Complex of the reaction DPA + **III**	198.35	167.83	273.57
para-σ-Complex (**V**) of the reaction DPA + **III**	171.26	166.72	246.82

Table 2

Cationic localization energies on diphenylamine azo coupling with substituted benzenediazonium cations

Cation	Diphenylamine molecule position	$\Delta\Delta H_f$, kcal/mol	$\Delta\Delta G_f$, kcal/mol
I	*Para*	16.05	3.51
II	*Para*	21.33	9.72
III	*Ortho*	17.06	4.63
III	*Meta*	−9.74	−22.17
III	*Para*	17.34	4.58

When taking into consideration the factors related to the electron structure of initial reactants and intermediates, one is led to the conclusion (Table 2) on equally possible attacks at *ortho* and *para* positions of DPA molecule by the cation **III**.

To incorporate the effect of aqueous medium in the regioselectivity of DPA azo coupling with the cation **III**, we referred (analogously to[21-28]) to clusters that include the σ-complexes (**IV**, **V**) occurring on the electrophilic attack at *ortho* (**IV**) and *para* (**V**) positions of DPA molecule by the cation **III**, and 157 water molecules.

We have evaluated semiquantitatively the aqueous medium influence on the state of dissolved molecular systems (M) with the help of a value estimating the energetic effect of the interaction of the molecule M with an ensemble (*m*) of water molecules; such a value has the physical meaning of hydration enthalpy:

$$\Delta H_{aq} = \Delta H_f(M \cdot mH_2O) - \Delta H_f(M) - \Delta H_f(mH_2O).$$

The greater number of water molecules built in cluster, up to 729 in cubic cell with 28.00 Å side, that corresponds to liquid water density,[29] the more adequately aqueous medium is considered. In our case, density of water molecules distribution in a cell approaches to this value for liquid state, even a partial occupation of the cell volume by the σ-adduct **IV** or **V** is left disregarded. Thus, for the cluster **IV**·157H$_2$O, the *HyperChem* cubic cell side consists 17.139 Å, the water molecules quantity per the unit of volume for cubic cell is 0.0312 Å^{-3}, and the gradient norm after the quantum chemical computation is equal to 0.872 kcal/(mol·Å). The corresponding values for the supermolecule **V**·157H$_2$O are 17.133 Å, 0.0312 Å^{-3}, and 0.968 kcal/(mol·Å), respectively. As the literature[29] data for the cluster 729H$_2$O show, cubic cell with the side 28.000 Å containing liquid H$_2$O is featured by 0.0332 water molecules per the unit of cell's volume.

By means of the ΔH_{aq} values (*m* = 157) comparison, it has been elucidated that the formation of *para*-σ-adduct **V** is 22.4 kcal/mol more favourable, than of *ortho*-σ-complex **IV**. Therefore, aqueous medium stabilizes predominantly the intermediate **V**, choosing between two alternative routes of azo coupling. The reaction product is of the structure given below:
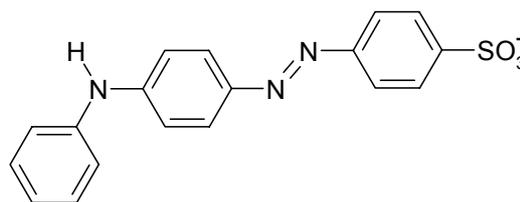
The quantum chemical prediction based on the idea of *para* isomeric σ-complexes formation as the intermediates, on the knowledge of kinetic control of azo coupling reactions[16, 17, 21, 22] and, consequently, on the analysis of the $\Delta\Delta H_f$ and $\Delta\Delta G_f$ values computed for isolated molecular systems, leads to the series **II** > **III** ⪸ **I** for the rates of coupling with the corresponding diazonium cations involved. Such result coincides well with the experimentally found[1] succession for the reactions in aqueous medium.

Rate constant *k* is related to activation energy E_a by Arrhenius equation[30]

$$k = A\exp(-E_a/RT),$$

where *A* is an exponential multiplier. Provided that the reactions under study are kinetically controlled,[16, 17, 21, 22] the linear dependences ln*k* vs $\Delta\Delta H_f$ and ln*k* vs $\Delta\Delta G_f$ would be expected.

Indeed, as concerned to the reactions in the aqueous solution, we have shown that for the ln*k vs*

$\Delta\Delta H_f$ and $\ln k$ vs $\Delta\Delta G_f$ linear interrelationships, the correlation coefficients (r) are 0.9895 and 0.9975, respectively. The more rigorous dependence ($\ln k$ vs $\Delta\Delta G_f$) with account for the entropy contribution to the free energy, the higher the r value.

For the number of points equal to three, the correlation coefficient's deviation from zero is significant in the only case of its strict equality to unity.[31] However, the sufficiently high r values attest to the fact that the correlations obtained have a not random nature.

According to,[1] micellar medium retards the reaction of DPA with aryldiazonium **III**, compared to the aqueous solution, whereas the DPA reaction with the cations **I**, **II** is accelerated, conversely, in going from aqueous medium to micellar one. Starting from the notion of "micellar catalysis",[32, 33] as well as from the ideas outlined in the works[34, 35] and references cited therein, the author of[1] has explained the aforesaid by the fact that the zwitterionic form **III**, in contrast to the cations **I**, **II** and the protonated form of DPA, does not concentrate in micelles of surfactant.

The values of $\lg P$ (P is a distribution coefficient in the system of 1-octanol - water, that serves the commonly accepted measure of hydrophobicity) we computed by the atomic-bond-additive scheme[10-13] appeared to be equal to 1.45, 1.70 and 1.13 for the diazonia **I**, **II** and **III**, respectively.

Consequently, the series of decelerating rates of DPA azo coupling in micellar medium[1] (**II** > **I** > **III**) coincides to the series of decreasing hydrophobicity of the aryldiazonium cations.

In accordance with the law of mass action,[30] the reaction rate is proportional to the reactants' concentrations, the latter linearly depending on the distribution coefficient P. Thus one can expect a linear relation between the rate constant k and the P value. For the micellar medium, such a dependence exists really, and $r = 0.9931$.

It is apparent that the more hydrophilic is diazonium, the weaker is its tendency to concentrate in micelle of surfactant, and to the greater extent its hydrate shell prevents the electrophilic attack to DPA molecule formed as a result of deprotonation of the diphenylammonium cation in micelle.

Obviously, the substantial contribution to the reactivity of the cations **I-III** on their interaction with DPA is made by medium (aqueous and micellar).

At the condition of the experimental and computational data array accumulation, $\ln k$ vs $\Delta\Delta H_f$, $\ln k$ vs $\Delta\Delta G_f$ and k vs P correlations similar to the aforesaid ones, would be fit for *a priori* rate con-

stants predictions for the reactions of DPA and other azo components with various benzenediazonia and other aryldiazonium cations.

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