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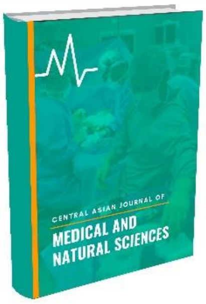

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DIAZOTIZATION OF p- AND m-FERROTSENYLBENZOIC ACIDS WITH p-AMINOPHENOL AND STUDY OF THE EFFECT OF SOLUTIONS ON PRODUCT YIELD

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ABSTRACT: The article presents the results of studying the reaction of diazotization of p- and m-ferrocenylbenzoic acids with p-aminophenol and the catalytic effect of solvents on the yield of the products of these reactions by the method of quantum-chemical calculation.

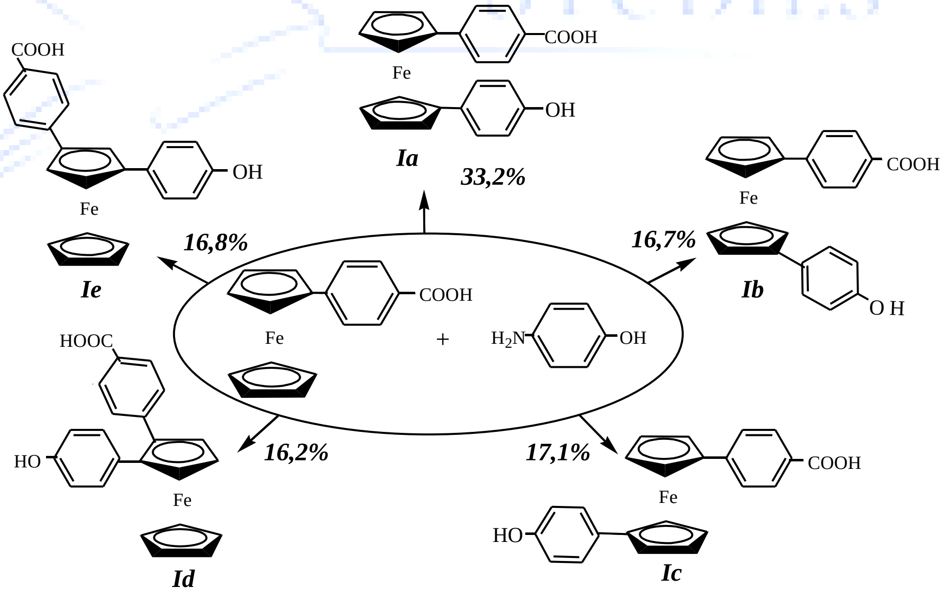
KEYWORDS: Ferrocene, ferrocenbenzoic acids, p-aminophenol, diazotization reaction, chloroform, diethyl ether, quantum chemical calculation, activation energy, product yield, enthalpy changes.

INTRODUCTION

To date, ferrocene and its derivatives, a typical representative of sandwich-metal-organic compounds, have been synthesized in various ways. [1,2]. The composition, structure, physicochemical properties and many other properties of the obtained substances have been studied in depth. The results of the research showed that ferrocene and most of its derivatives are chemically stable and physiologically active compounds [3,4]. In particular, compounds of ferrocene obtained by diazotization with m- and p-aminobenzoic acids, p-aminophenol and its derivatives were found to be stable. These diazotization reactions were carried out in a diethyl ether medium in the presence of a mixture of sodium nitrite, hydrochloric acid, sodium acetate and urea, which decompose excess nitric acid. The result made a mixture of mono- and small-scale di-exchanged products [5, 6]. The synthesized ferrocene benzoic acids and their derivatives with several substances such as urea, thiourea were obtained. The results of laboratory and field studies have shown that the obtained products have a high physiological activity. Some of the compounds with the highest physiological activity have been recommended for use as plant-enhancing biostimulants [7,8]. However, the diazotization reaction of ferrocene benzoic acid isomers with aminophenols has not been performed, mixed substituted di-exchange products containing carboxyphenyl and oxyphenyl have not been obtained, and their structure has not been studied.

This paper presents the results of quantum chemical calculations performed to study the diazotization reactions of ferrocene with p-aminobenzoic acid and p-aminophenol, as well as to determine the effect of solvents on the reaction product structure optimization and yield.

It is known from textbooks that similar diazotic reactions can result in large amounts of di-, as well as small amounts of tri- and poly-exchange products [3]. In this paper, we present an analysis of the results obtained by quantum chemical calculations of the theoretical structure and energy characteristics of various isomers of a di-exchanged product that can only be formed as a result of a reaction between p-ferrocenylbenzoic acid and p-aminophenol. The Hartry energies of the optimized molecular structures of the possible ***Ia, Ib, Ic, Id***, and ***Ie*** of the di-exchanged products were calculated. The calculations were performed using the Gaussian 98 [9] software package *DFT / B3LYP* hybrid method on the basis of *3-21G* using the *Opt* method to optimize the structure of the initial, intermediate and product molecules of the reaction. The *TS* transition state of the reaction was determined using the Bernie method.



Picture 1. Di-exchange products that can be formed by the diazotization reaction of p-ferrocenylbenzoic acid with p-aminophenol

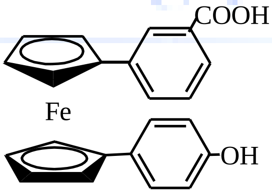
The results of the calculations are presented in Table 1 below.

Table 1

Hartry energies of di-exchanged products and the differences between them

State	**Substance**	***E*$_{Hart}$*, кJ/mol***	***ΔE, (J)*** *(In relation to **Ia**)*	Percentage of substance, (%)
Heteroannular	***Ia***	**-6206,04**	**0**	**33,2**
	Ib	-6205,963	92,6	16,7
	Ic	-6205,966	89	17,1
Homoannular	***Id***	-6205,952	105	16,2
	Ie	-6205,962	93,7	16,8

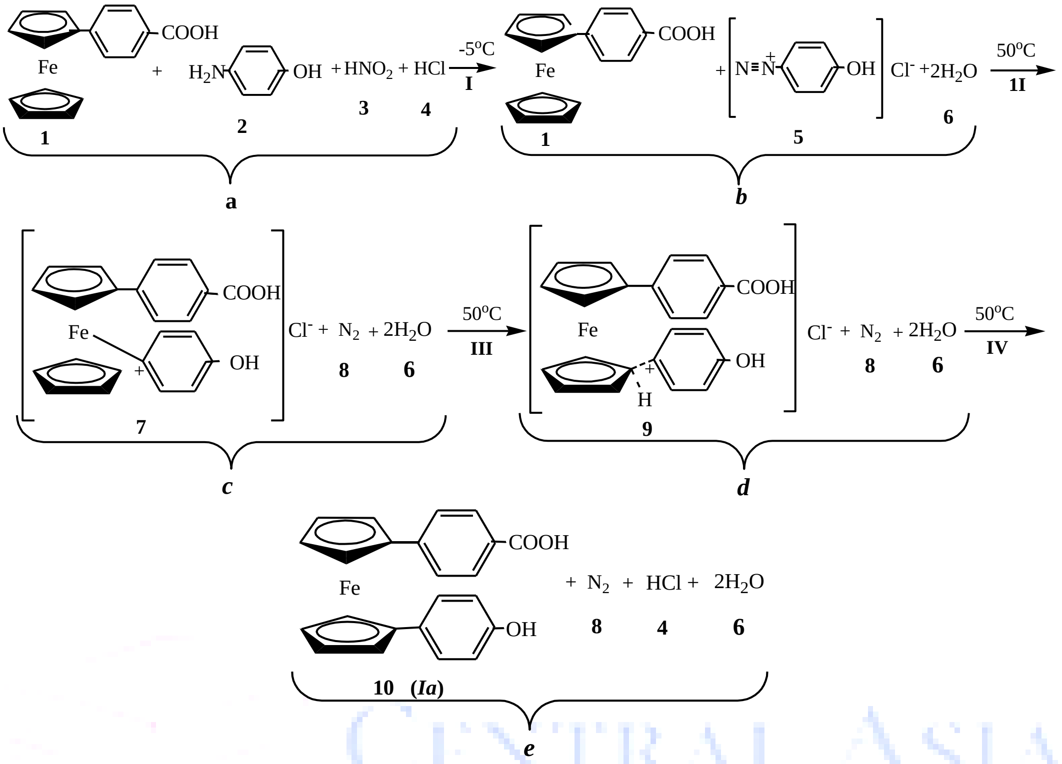
Using the above quantum chemical method, the values of enthalpy change (*ΔH* and *ΔH′*) for the formation reaction of each substance (***Ia, Ib, Ic, Id*** and ***Ie***) shown in Picture 1 are determined based on their dependence on the equilibrium constant of the reaction, in which case the proportion of each substance relative to the mixture of di-exchanged products was calculated. The results of the calculations show that among the molecular structures in Picture 1, the ***Ia*** structure occupies the most energetically favorable and stable state relative to the others (i.e., ***Ib, Ic, Id***, and ***Ie***). This means that the di-exchange main product (**33.2%**) formed by the diazotization reaction of p-ferrocenylbenzoic acid with p-aminophenol has a heteroannular structure, bis-1- (4-carboxyphenyl) -1 '- (4-oxy- phenyl) can be a theoretical basis for the conclusion that the molecular structure of ferrocene is fully consistent with ***Ia***. A similar study was conducted for the products of the diazotization reaction between m-ferrocenylbenzoic acid and p-aminophenol. Among the products, the molecular structure of bis-1- (3-carboxyphenyl) -1 '- (4-oxy-phenyl) (***IIa***) found to be energetically stable relative to the products [10].



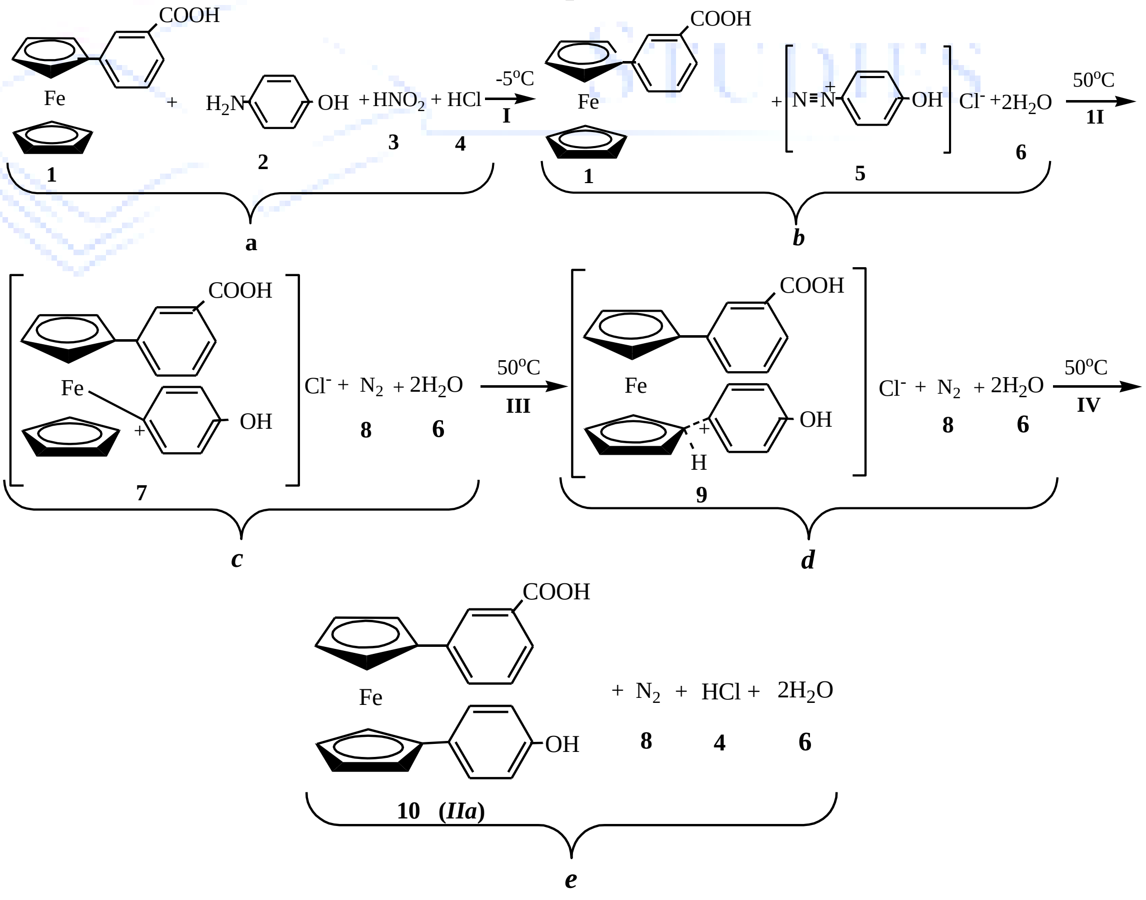
Picture 2. Molecular structure of bis-1- (3-carboxyphenyl) -1 '- (4-oxy-phenyl) (*IIa*).

The results of the study show that the above reaction method can also be used for diazotic reactions between ferrocenylbenzoic acids and other isomers of aminophenols.

Experimental studies carried out quantum chemical calculations to theoretically substantiate that the product yield in the chloroform medium is higher than in the diethyl ether medium as a result of diazotization reactions of p- and m-ferrocenylbenzoic acids with p-aminophenol. For this purpose, the mechanisms of diazotization reactions between p- and m-ferrocenylbenzoic acid and p-aminophenol, consisting of four separate stages (**I, II, III, IV**) were developed, five systems (***a, b, c, d, e***) for both (**A** and **B**) reactions were formed. The Hartry energies of the molecules in each system were then determined separately in the diethyle ether and chloroform medium using the quantum chemical calculation method described above. The energy of each system was generated from the sum of the Hartry energies of the molecules in it (Tables 2 and 3). Using the energies of the systems, the TS transition states of reactions **A** and **B** were determined by the Bernie method.



Picture 3. Mechanism of diazotization (A) reaction between p-ferrocenylbenzoic acid and p-aminophenol.



Picture 4. The mechanism of the diazotization (B) reaction between m-ferrocenylbenzoic acid and p-aminophenol.

Table 2

Hartry energies of substances and systems shown in Picture 3

System	Matter	Amount	*Reaction environment*			
			Diethyl ether		*Chloroform*	
			Hartry energy of matter, (*kJ*)	Hartry energy of the system, (*kJ*)	Hartry energy of matter, (*kJ*)	Hartry energy of the system, (*kJ*)
a	**1**	1	-5404,955	-8088,164	-5404,957	-8088,167
	2	1	-945,416		-945,417	
	3	1	-535,769		-535,774	
	4	1	-1202,022		-1202,031	
b	**1**	1	-5404,955	-8088,725	-5404,957	-8088,747
	5	1	-2285,77		-2285,780	
	6	2	-397,999		-398,01	
c	**7**	1	-7403,523	-8085,474	-7403,550	-8085,518
	8	1	-283,952		-283,958	
	6	2	-397,999		-398,01	
d	**9**	1	-7403,543	-8085,494	-7403,762	-8085,730
	8	1	-283,952		-283,958	
	6	2	-397,999		-398,01	
e	**10**	1	-6205,245	-8089,219	-6205,357	-8089,236
	8	1	-283,952		-283,958	
	4	1	-1202,022		-1202,023	
	6	2	-397,999		-398,01	

The fact that the Hartry energy difference of the systems is higher than the others in the second stages of the above reactions, transitioning from ***b*** to ***c***, indicates that these stages are the slowest stages and determines the basic transition state of both reactions. Also, the difference (*kJ/mol*) between systems ***a*** and ***c*** of reactions **A** and **B** indicates the value of the activation energies of these reactions **A** and **B**.

Table 3

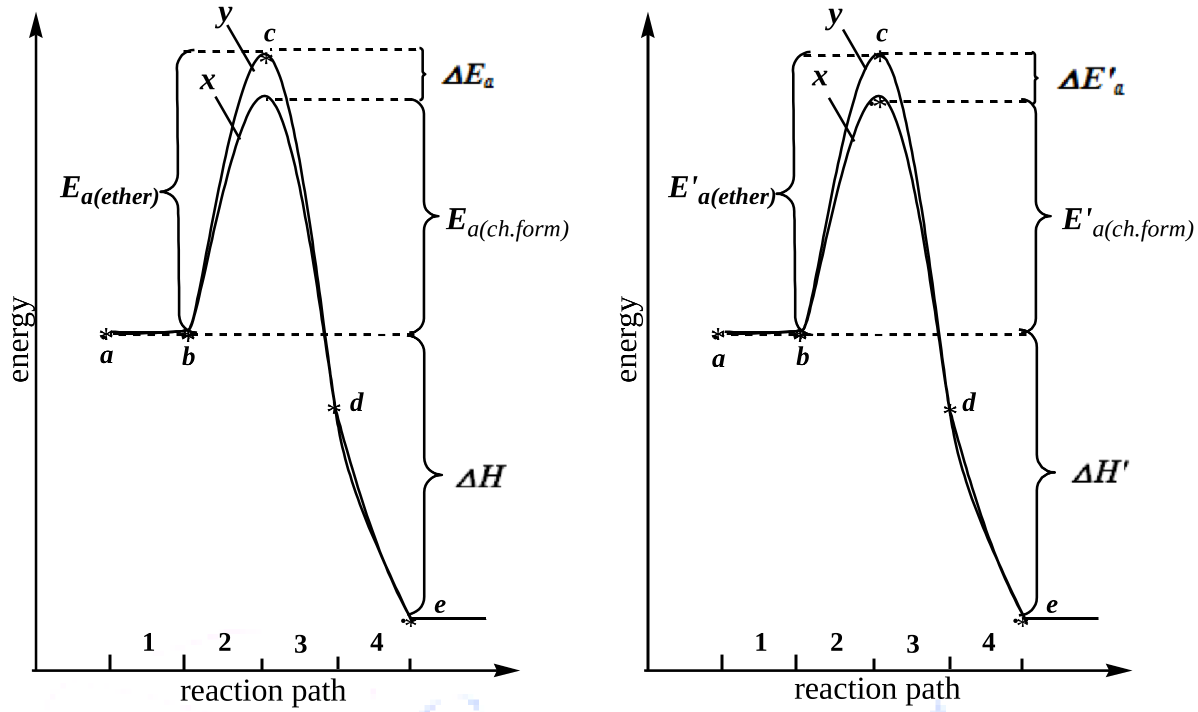
Hartry energies of substances and systems shown in Picture 4

			Reaction environment	
			Diethyl ether	*Chloroform*

System	Matter	Amount	Hartry energy of matter, (*kJ*)	Hartry energy of the system, (*kJ*)	Hartry energy of matter, (*kJ*)	Hartry energy of the system, (*kJ*)
a	**1**	1	-5405,007	-8088,217	-5405,008	-8088,218
	2	1	-945,416		-945,417	
	3	1	-535,769		-535,774	
	4	1	-1202,022		-1202,031	
B	**1**	1	-5405,007	-8088,777	-5405,008	-8088,798
	5	1	-2285,77		-2285,780	
	6	2	-397,999		-398,01	
C	**7**	1	-7403,77	-8085,724	-7403,812	-8085,781
	8	1	-283,952		-283,958	
	6	2	-397,999		-398,01	
D	**9**	1	-7403,794	-8085,746	-7403,815	-8085,783
	8	1	-283,952		-283,958	
	6	2	-397,999		-398,01	
E	**10**	1	-6205,306	-8089,805	-6205,31	-8089,953
	8	1	-283,952		-283,958	
	4	1	-1202,022		-1202,023	
	6	2	-397,999		-398,01	

Furthermore, the difference between the energies of the Hartry energies of the systems ***a*** and ***e*** of each reaction (kJ / mol) determines their enthalpy value. Based on the results obtained, TS transition state diagrams were constructed using energy changes in each (**I-IV**) stage of diazotization (**A** and **B**) reactions between p- and m-ferrocenylbenzoic acids and p-aminophenol in the above diethyle ether and chloroform medium (Picture 5).

From the figure above, the values of the activation energies of reactions **A** and **B** in the chloroform medium ($E_{a(ch.form)}$ and $E'_{a(ch.form)}$), the activation energies in the diethyle ether medium are ($E_{a(ether)}$ 50,6 J/mol and $E'_{a(ether)}$) 56 J/mol respectively. This situation theoretically explains the fact that the yield of products is 7-8% higher than that of diethyl ether when the actual synthesis reactions are carried out in a chloroform environment.



The transition state of A reaction **The transition state of B reaction**

Picture 5. TS transition mode diagram of diazotization reactions between p- and m-ferrocenylbenzoic acids and p-aminophenol.

Where ***x*** is the transition state of the reaction in the chloroform medium; ***y*** is the transition state of the reaction in a diethyl ether medium; $E_{a(ether)}$ = 2,689kJ/mol; $E_{a(ch.form)}$ = 2,648kJ/mol; ΔE_a = 50,6J; ΔH = - 1,055kJ/mol; $E'_{a(ether)}$ = 2,493kJ/mol; $E'_{a(ch.form)}$ = 2,437kJ/mol; $\Delta E'_a$ = 56J; $\Delta H'$= - 1,06kJ/mol.

CONCLUSIONS

The results of quantum chemical calculations showed that the activation energies of diazotization reactions between p- and m-ferrocenylbenzoic acids and p-aminophenol are significantly reduced compared to diethyl ether when conducted in a chloroform medium. This serves as a clear example of the fact that the reaction rate between substances, and on this basis the yield of products, is also significantly affected by the nature of the solvent.

Thus, in practice, it can be concluded that the products of diazotization reactions between p- and m-ferrocenylbenzoic acids and p-aminophenols increased by 7-8% in chloroform compared to the diethyl ether medium due to a slight decrease in reaction activation energies.

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