QUANTUM-CHEMICAL MODELING OF HYDROSILYLATION REACTION OF TRIETHOXYSILANE TO DIVINYLBENZENE

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Abstract. Hydrosilylation of triethoxysilane with the mixture of ortho- and para-divinylbenzene in the presence of Karstedt's catalyst has been carried out and the corresponding product triethoxy(vinylphenethyl)silane have been obtained. The structure and composition of the obtained product were proved by means of determining molecular mass, molecular refraction, and ^{1}H and ^{13}C NMR spectra data. It was found that the addition reaction proceeds both in ortho-position as well as in para-position. Hydrosilylation proceeds both Markovnikov and anti-Markovnikov rule. Via quantum-chemical calculations using the non-empirical density functional theory (DFT) method, the possible direction of the reaction has been considered.

Keywords: Alkylation reaction, FTIR, ^{1}H and ^{13}C NMR spectroscopy, DFT.

1. Introduction

In recent years great interest in the development of new composites derived from thermoplastic polymer matrices reinforced with wood filler, because of their environmental and economic benefits.[1-5] Their renewability, biodegradability, low density, high stiffness, and relatively low price make them interesting.[6,7] Among these various thermoplastic matrices mainly used in the manufacture of plastic/wood composites the most popular was polystyrene[8] because of its inapparency, fluidity, and good electrical insulating properties.[9]

Trialkoxy(4-vinylphenethyl)silane (StSi(OR)$_3$) type monomers were synthesized *via* two-step reactions: hydrosilylation reaction of 1.4-divinylbenzene with trich-

lorosilane, followed by esterification reactions with primary alcohols.[10,11] The yield of trialkoxy group-containing compounds is about 50 %.

The aim of our work is to investigate the hydrosilylation reaction of triethoxysilane with the mixture of ortho- and para-divinylbenzene and predict the direction of this reaction using the non-empirical density functional theory (DFT).[12] Density functional theory (DFT) is widely applied to both molecules and materials, but well-known energetic delocalization and static correlation errors in practical exchange-correlation approximations limit quantitative accuracy.[13-19]

2. Experimental

2.1. Materials

All synthetic manipulations were carried out under an atmosphere of dry nitrogen gas. All solvents were degassed and purified prior to use according to standard literature methods: toluene, hexane, and tetrahydrofuran were distilled from sodium/benzophenone ketyl. All other reagents styrene, vinyl triethoxysilane, and AlCl$_3$ purchased from Aldrich were used as received or distilled prior to use.

2.2. Characterization

FTIR spectra were recorded on a Nicolet Nexus 470 machine with MCTB detector (KBr, cm^{-1}). ^{1}H, ^{13}C NMR spectra were recorded on a Bruker ARX400 NMR spectrometer at a 400-MHz operating frequency with CDCl$_3$ as the solvent and an internal standard.

2.3. Hydrosilylation Reaction of Triethoxysilane with Divinylbenzene

In a three-necked flask connected with a backflow condenser and dropping funnel, 50.0 g (0.48 mol) of mixture of ortho- and para-divinylbenzene was placed. Using the dropping funnel 91.3 g (0.48 mol) of triethoxysilane with 2-3 drops of Karstedt's catalyst were added under constant stirring. The mixture was heated for 3 h in

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313–323 K temperature range up to disappearing of the characteristic signal of ≡Si-H bond in FTIR spectra. After completion of the hydride addition 2-3 g of activated carbon were added, filtered, and distilled in the vacuum of 1–2 Hg. After distillation of 90 g viscous transparent product, 45 g (55 %) of products have been obtained.

3. Results and Discussion

Hydrosilylation reaction of triethoxysilane to divinylbenzene at 1:1 ratio of initial compounds in the presence of Karstedt's catalysts has been carried out, investigated and corresponding addition products have been obtained. The hydrosilylation reaction proceeds according to the Scheme 1:
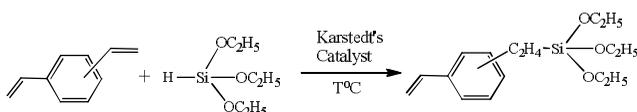
Scheme 1. Hydrosilylation reaction of triethoxysilane with divinylbenzene

In the ^{1}H-NMR spectrum of compound (Fig. 2), a multiplex signal is observed in the $-C\underline{H}_2Si\equiv$ fragment for methylene protons, with a center of chemical shift $\delta \approx 1.08$ ppm, and a multiplet signal for protons in the methylene group in the fragment $-ArC\underline{H}_2-$ with the center of chemical shift $\delta \approx 2.38$ ppm, which is formed by a hydrosilylation reaction of a mixture of ortho- and para-divinylbenzene with triethoxysilane according to the anti-Markovnikov rule. The spectrum shows a multiplet signal for methyl protons with the center of chemical shift at $\delta \approx 1.49$ ppm in the fragment $\equiv CH-\underline{CH}_3$ and signal for methin proton with the center of chemical shift $\delta \approx 2.78$ ppm, generated by hydrosilylation reaction of triethoxysilane with the mixture of ortho- and para-divinylbenzene according to the Markovnikov rule. Thus the content of the Markovnikov addition product in the hydrosilylation product is 12–15 %. The multiplet signals with the center of chemical shift $\delta \approx 1.36$, 3.87 ppm correspond to the protons in the fragment $-CH_2-C\underline{H}_3$ and $-O-C\underline{H}_2-$. Signals with a chemical shift $\delta \approx 5.30$ and 5.79 ppm correspond to protons in the methylene fragment in the cis- and trans- state $C\underline{H}_2=CH-$. And the multiplet signal with the center of chemical shifts of $\delta \approx 6.79$ ppm corresponds to the methin protons in the fragment $CH_2=C\underline{H}-$. Multiplet signals $\delta \approx 7.32–7.49$ ppm correspond to ortho- and para-substituted phenyl protons.

The structure and composition of triethoxy(vinylphenethyl)silane were proved *via* the determination of molecular masses, molecular refraction, FTIR, ^{1}H, and ^{13}C NMR spectra data.

In the FTIR spectra of triethoxy(vinylphenethyl)silane (Fig. 1), the absorption bands at 755 and 776 cm^{-1} characteristic of disubstituted benzene rings are observed. Doublet absorption bands are also observed at 963–980 cm^{-1}, which are characteristic for the Si–OCH$_2$CH$_3$ group, for the (Si–OC) bond in the 1100 and 1165 cm^{-1} region, and also, 1290 (Si–C), 1389 (CH=CH$_2$), and 2800–3100 cm^{-1} (CH). The spectrum also shows the characteristic doublet absorption band C=C of the aromatic nucleus with a maximum of 1650-1654 cm^{-1}.
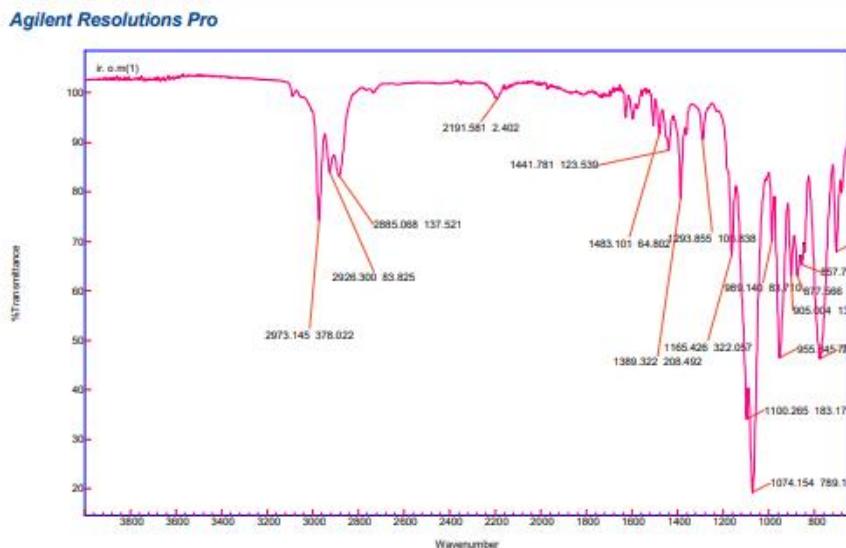
Fig. 1. FTIR spectra of triethoxy(vinylphenethyl)silane
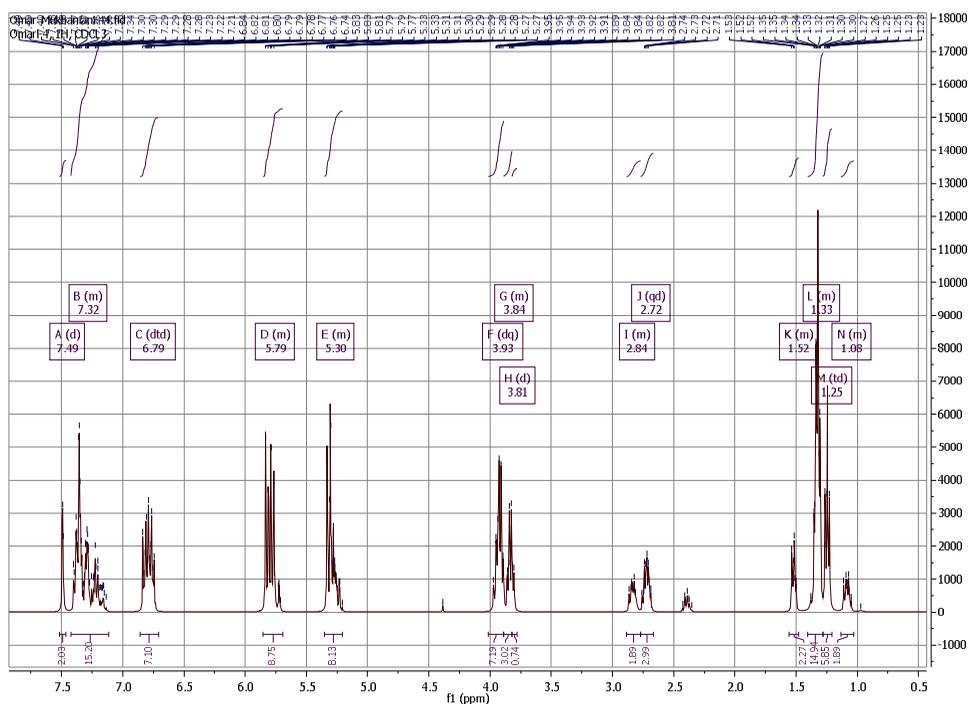
Fig. 2. ^{1}H NMR pectrum of triethoxy(vinylphenethyl)silane
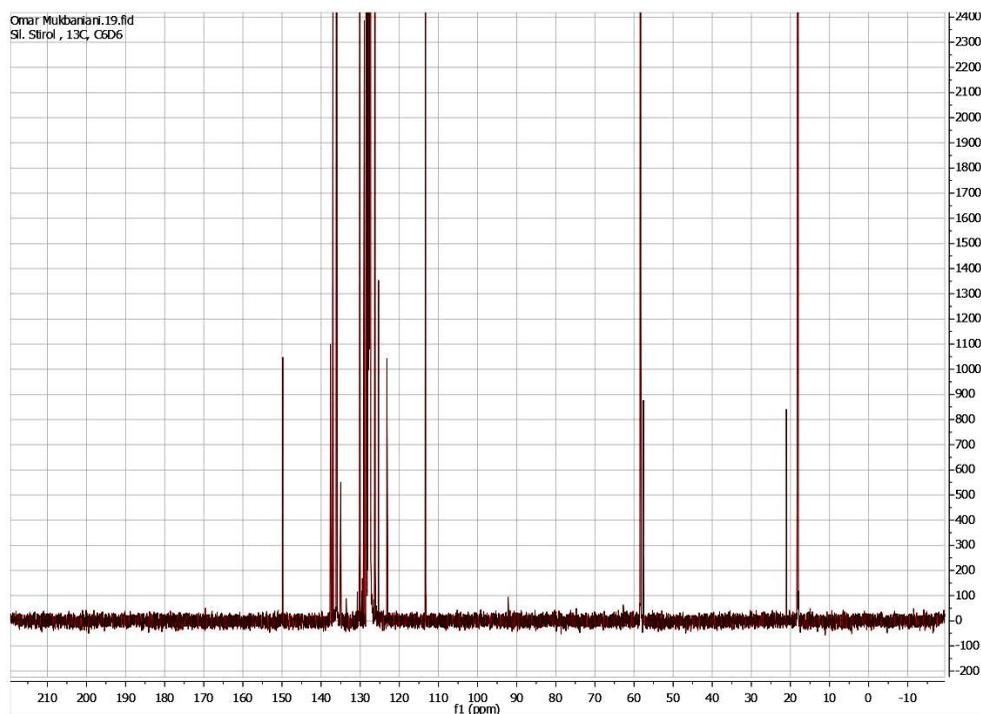
Fig. 3. ^{13}C NMR spectrum of triethoxy(vinylphenethyl)silane

In ^{13}C NMR (*d*-benzene), triethoxy(vinylphe-nethyl)silane (Fig. 3) one can see the following signal with chemical shifts at (ppm), δ=18.8 (CH$_2$C$\underline{H}_3$); signal for δ=17.5 (Si-$\underline{C}$H$_2$); 28.8 (O –$\underline{C}$ H$_2$); 57.8 (C$_6$H$_4$-$\underline{C}$H$_2$); 112.1 (=$\underline{C}$H$_2$); 125-128 (for phenyl carbon nuclear); 138 (=$\underline{C}$H). For obtaining compound ^{13}C NMR spectra are in accordance with ^{1}H NMR spectra.

Fig. 4 shows the hetero cozy NMR spectra of triethyl(vinylphenyl)silane, where ^{1}H and ^{13}C spect-ra correlate with each other.
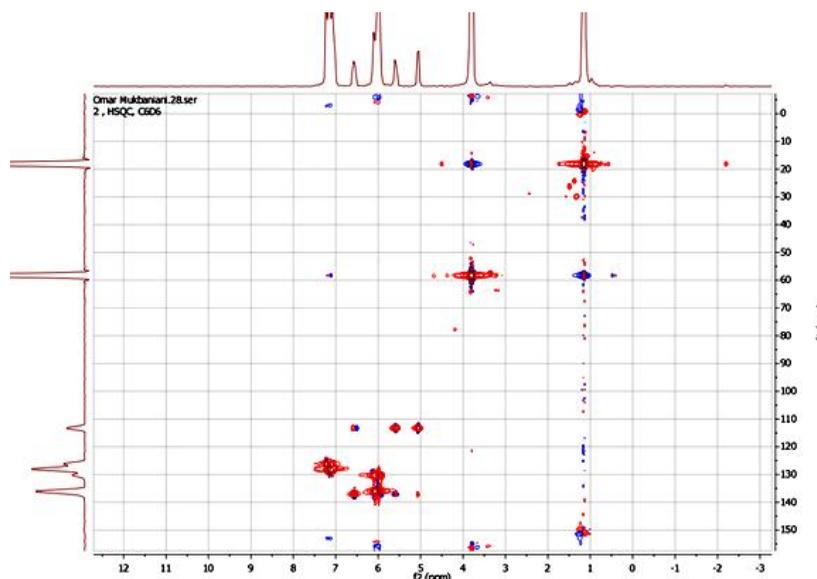
Fig. 4. Cozy spectra of triethoxy(vinylphenethyl)silane
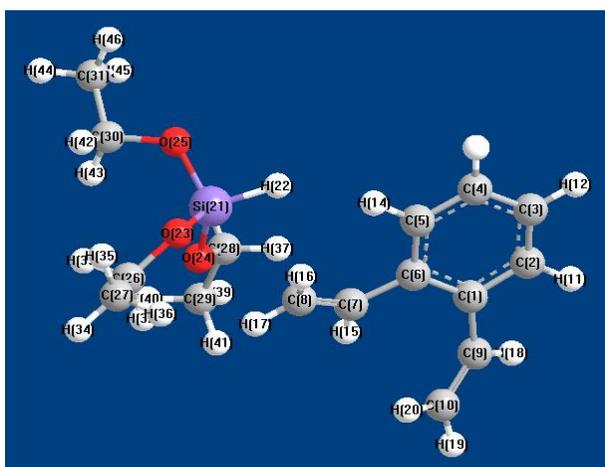
Fig. 5. Initial state of the system in the model hydrosilylation reaction of triethoxysilane with ortho-divinylbenzene according to the anti-Markovnikov rule
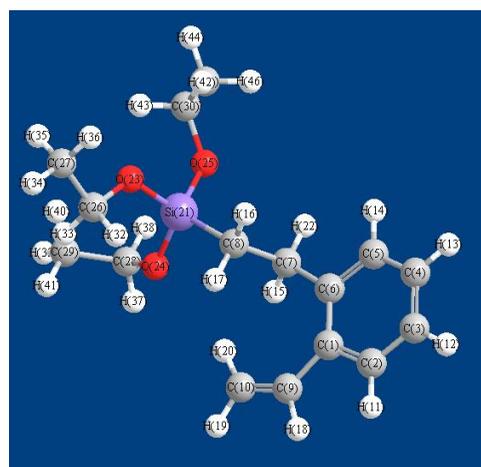
Fig. 6. Final state of the system in the model hydrosilylation reaction of triethoxysilane with ortho-divinylbenzene according to the anti-Markovnikov rule

For a detailed study of the direction of the hydro-silylation reaction, we studied quantum-chemical calculations, which were performed using the non-empirical density functional theory (DFT).[12] For this calculation the program "Priroda-04" was used.[12]

Hydrosilylation reactions in ortho- and para-di-vinylbenzene were discussed, both according to Markovnikov and anti-Markovnikov rules.

The distance between the carbon and silicon atoms was taken to be 1.0 Å longer than the bond distance in the final product. The distances between the atoms varied at intervals of 0.05 Å. The initial states of the systems are given in Figs. 5, 8, 11, and 14, and the final states are given in Figs. 6, 9, 12, and 15. The dependence of the energy change (ΔE) of the systems on the distances between the atoms is given in Figs. 7, 10, 13, and 16.

As can be seen from Fig. 7, during approaches of the silicon Si_{21} to carbon C_8 atom at a distance of $R_{Si_{21}-C_8} = 2.18$ Å, the system energy increases. Simultaneously the bond order between the C_7 and C_8 atoms in the ortho-divinylbenzene molecule decreases from 1.73 up to 1.32, and between the Si_{21} and H_{22} atoms in the triethoxysilane molecule from 0.92 to 0.76. New bonds are observed ($P_{Si_{21}-C_8} = 0.30$ and $P_{C_7-H_{22}} = 0.12$). The double bond moves to a single C-C bond. The hydrogen atom completely turns from the silicon Si_{21} atom ($P_{Si_{21}-H_{22}} = 0.00$) and joins the carbon C_7 atom ($P_{C_7-H_{22}} = 0.96$).
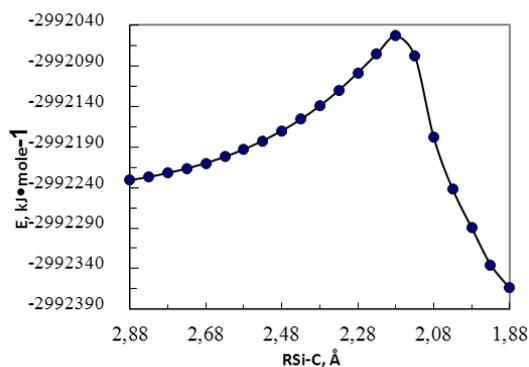
Fig. 7. Dependence of the energy change (ΔE) of the system on the distance between Si_{21}-C_8 atoms (R_{Si-C}) in the current model reaction of triethoxysilane with ortho-divinylbenzene according to the anti-Markovnikov rule

Activation energy $\Delta E^{\#} = 177.60$ kJ/mol, and heat effect of reaction $\Delta E = -132.77$ kJ/mol. As we can see, the reaction is exothermic.

Given that the system has 4 reaction centers [broken bonds (2): $C_7 = C_8$, Si_{21}-H_{22}; Generated bonds (2): Si_{21}-C_8, C_7-H_{22}], the said activation energy must be divided by 4. In this case, the activation energy calculated for one reaction center is $\Delta E^{\#} = 177.60$ kJ/mol/4 = = 44.4 kJ/mol, which means that the obtained value corresponds to the energy characteristic of the chemical reactions.

As it's seen from Fig. 10, during approaches of the silicon Si_{21} to carbon C_7 atom at a distance of $R_{Si_{21}-C_7} = 2.20$ Å, the system energy increases. Simultaneously the bond order between the C_7 and C_8 atoms in the ortho-divinylbenzene molecule decreases from 1.73 up to 1.19, and between the Si_{21} and H_{22} atoms in the triethoxysilane molecule from 0.92 to 0.70. New bonds are observed ($P_{Si_{21}-C_7} = 0.19$ and $P_{C_8-H_{22}} = 0.22$). The double bond moves to a single C-C bond. The hydrogen atom completely turns from the silicon Si_{21} atom ($P_{Si_{21}-H_{22}} = 0.00$) and joins the carbon C_8 atom ($P_{C_8-H_{22}} = 0.91$).

Activation energy $\Delta E^{\#} = 190.93$ kJ/mol, and heat effect of reaction $\Delta E = -22.18$ kJ/mol. As we can see, the reaction is exothermic.
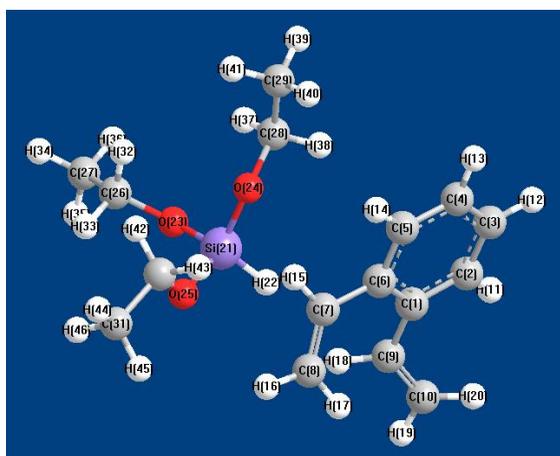
Fig. 8. Initial state of the system in the model hydrosilylation reaction of triethoxysilane with ortho-divinylbenzene according to the Markovnikov rule
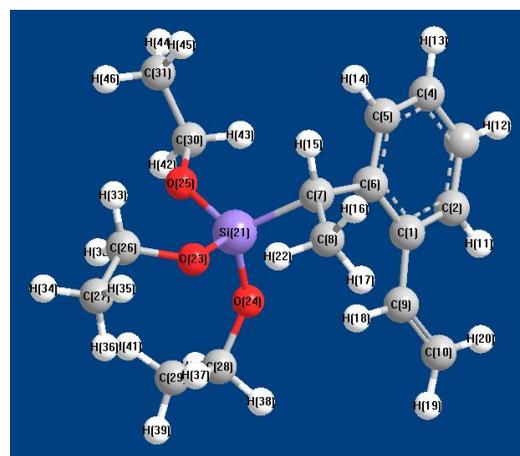
Fig. 9. Final state of the system in the model hydrosilylation reaction of triethoxysilane with ortho-divinylbenzene according to the Markovnikov rule

Fig. 10. Dependence of the energy change (ΔE) of the system on the distance between Si_{21}-C_7 atoms (R_{Si-C}) in the model hydrosilylation reaction triethoxysilane with ortho-divinylbenzene according to the Markovnikov rule
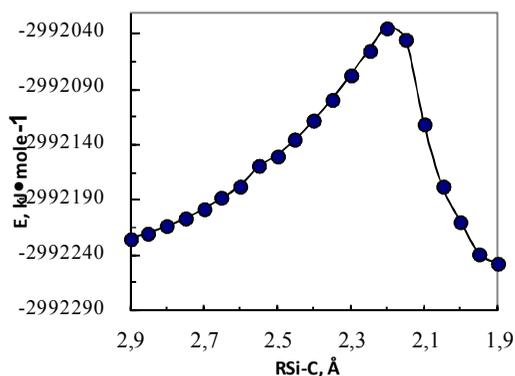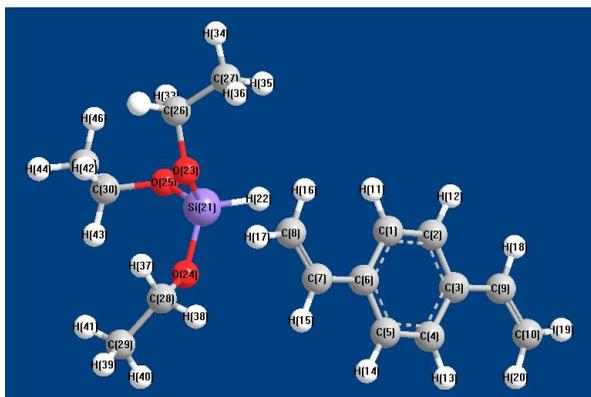
Fig. 11. Initial state of the system in the model hydrosilylation reaction of triethoxysilane with para-divinylbenzene according to the anti-Markovnikov rule

Fig. 12. Final state of the system in the model hydrosilylation reaction of triethoxysilane with para-divinylbenzene according to the anti-Markovnikov rule

As the system has 4 reaction centers [broken bonds (2): $C_7 = C_8$, $Si_{21}-H_{22}$; Generated bonds (2): $Si_{21}-C_7$, C_8-H_{22}], the mentioned activation energy must be divided by 4. In this case, the activation energy calculated for one reaction center is $\Delta E^{\#} = 190.93$ kJ/mol/4 = 47.73 kJ/mol, which means that the obtained value corresponds to the energy characteristic of the chemical reactions.

Activation energy $\Delta E^{\#} = 175.15$ kJ/mol, and heat effect of reaction $\Delta E = -143.35$ kJ/mol. As we can see, the reaction is exothermic.

As the system has 4 reaction centers [broken bonds (2): $C_7 = C_8$, $Si_{21}-H_{22}$; Generated bonds (2): $Si_{21}-C_8$, C_7-H_{22}], the mentioned activation energy must be divided by 4. In this case, the activation energy calculated for one reaction center is $\Delta E^{\#} = 175.15$ kJ/mol/4 = 43.79 kJ/mol, which means that the obtained value corresponds to the energy characteristic of the chemical reactions.

As it's seen from Fig. 16, during approaches of the silicon Si_{21} to the carbon C_7 atom at a distance of $R_{Si_{21}-C_7} = 2.24$ Å, the system energy increases. Simultaneously the bond order between the C_7 and C_8 atoms in the para-divinylbenzene molecule decreases from 1.74 up to 1.25, and between the Si_{21} and H_{22} atoms in the triethoxysilane molecule from 0.91 to 0.67. New bonds are observed ($P_{Si_{21}-C_7} = 0.21$ and $P_{C_8-H_{22}} = 0.15$). The double bond moves to a single C-C bond. The hydrogen atom completely turns from the silicon Si_{21} atom ($P_{Si_{21}-H_{22}} = 0.00$) and joins the carbon C_8 atom ($P_{C_8-H_{22}} = 0.96$).

Fig. 13. Dependence of the energy change (ΔE) of the system on the distance between $Si_{21}-C_8$ atoms (R_{Si-C}) in model hydrosilylation reaction of triethoxysilane with para-divinylbenzene according to the anti-Markovnikov rule

As it's seen from Fig. 13, during approaches of the silicon Si_{21} to the carbon C_8 atom at a distance of $R_{Si_{21}-C_8} = 2.17$ Å, the system energy increases. Simultaneously the bond order between the C_7 and C_8 atoms in the para-divinylbenzene molecule decreases from 1.67 up to 1.33, and between the Si_{21} and H_{22} atoms in the triethoxysilane molecule from 0.92 to 0.73. New bonds are observed ($P_{Si_{21}-C_8} = 0.29$ and $P_{C_7-H_{22}} = 0.12$). The double bond moves to a single C-C bond. The hydrogen atom completely turns from the silicon Si_{21} atom ($P_{Si_{21}-H_{22}} = 0.00$) and joins the carbon C_7 atom ($P_{C_7-H_{22}} = 0.95$).

Activation energy $\Delta E^{\#} = 163.42$ kJ/mol, and heat effect of reaction $\Delta E = -131.77$ kJ/mol. As we can see, the reaction is exothermic.

As the system has 4 reaction centers [broken bonds (2): $C_7 = C_8$, $Si_{21}-H_{22}$; Generated bonds (2): $Si_{21}-C_7$, C_8-H_{22}], the mentioned activation energy must be divided by 4. In this case, the activation energy calculated for one reaction center is $\Delta E^{\#} = 163.42$ kJ/mol/4 = 40.86 kJ/mol, which means that the obtained value corresponds to the energy characteristic of the chemical reactions.

According to the values of the activation energy it is seen that energetically it is most convenient to join in the para state according to the Markovnikov's rule.
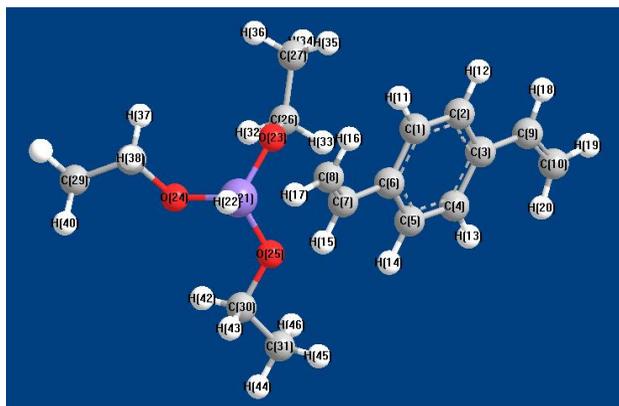
Fig. 14. Initial state of the system in the model hydrosilylation reaction of triethoxysilane with para-divinylbenzene according to the Markovnikov rule
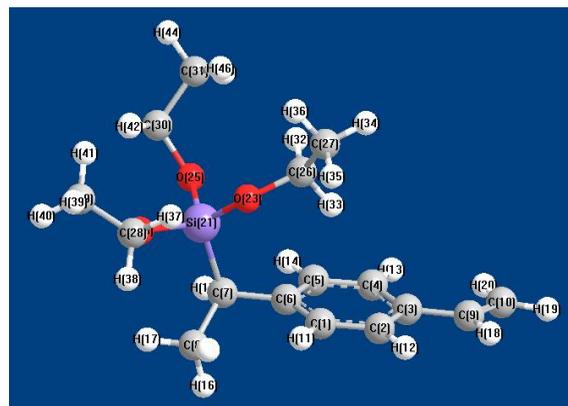
Fig. 15. Final state of the system in the model hydrosilylation reaction of triethoxysilane with para-divinylbenzene according to the Markovnikov rule

Fig. 16. Dependence of the energy change (ΔE) of the system on the distance between Si_{21}-C_7 atoms (R_{Si-C}) in the model hydrosilylation reaction of triethoxysilane with para-divinylbenzene according to the Markovnikov rule

So, referring to the NMR spectra data, we can conclude that the alkylation reaction proceeds with the formation of ortho- and para-addition mixture.

Acknowledgments
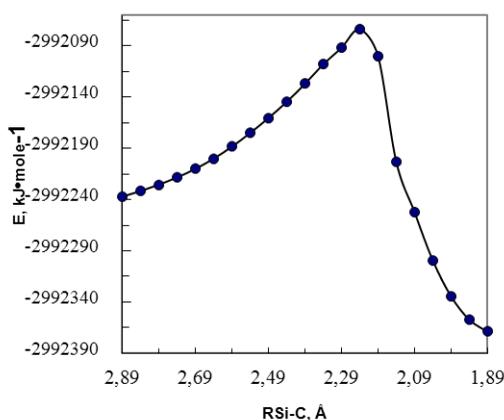
4. Conclusions

By the hydrosilylation reaction of triethoxysilane with divinylbenzene the alkylation product triethoxy (vinylphenethyl)silane has been obtained.

The structure and composition of the product were proved by determining the molecular mass, molecular refraction, FTIR, ^{1}H, and ^{13}C NMR spectroscopy.

For a detailed study of the direction of the alkylation reaction, we used quantum-chemical calculations, which were performed using the non-empirical density functional theory (DFT). According to the values of the activation energy, it is energetically most convenient to join in the ortho-state.

However, it's known that this method does not take into account the steric factors of the molecule caused by the ortho-addition of vinyltriethoxysilane to styrene.

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КВАНТОВО-ХІМІЧНЕ МОДЕЛЮВАННЯ РЕАКЦІЇ ГІДРОСИЛІЛУВАННЯ ДИВІНІЛБЕНЗЕНУ ТРИЕТОКСИСИЛАНОМ

Анотація. *Проведено гідросилілування триетокси-силаном суміші орто- і пара-дивінілбезену в присутності каталізатора Карстедта й отримано відповідний продукт – триетокси(вінілфенетил)силан. Будову і склад отриманого продукту підтверджено визначенням молекулярної маси, молекулярною рефракцією, а також даними ^{1}H i ^{13}C ЯМР-спектроскопії. Встановлено, що реакція приєднання відбувається як в орто-, так і в пара-положенні. Гідросилілування відбувається і за правилом Марковникова, і проти правила Марковникова. Можливий напрям реакції розглянуто через квантово-хімічні розрахунки з використанням неемпіричного методу теорії функціонала густини (DFT).*

Ключові слова: реакція алкілування, ІЧ-спектроскопія з перетворенням Фур'є, ^{1}H i ^{13}C ЯМР-спектроскопія, DFT.