

Production Of Vinyl Esters Based On Vinylation Of Ethanolamine With Acetylene

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Summary. Recently, a lot of scientific work has been carried out to create methods for producing vinyl compounds of substances containing active hydrogen atoms in superbasic systems. In this work, we studied the vinylation of monoethanolamine with acetylene in superbasic media. The effect of temperature, catalyst, reaction time, and other factors on the yield of vinyl ester of monoethanolamine has been studied. Also, quantum-chemical calculations theoretically calculated the active reaction centers of monoethanolamine, the distribution of atomic charges.

Keywords: monoethanolamine, vinylation process, vinyl ester, hydroxyl group, nucleophilicity, charge distribution, reaction time, yield of monoethanolamine vinyl ester.

Introduction. In recent years, the synthesis of new types of biologically active organic substances and the production of compounds with different properties based on them is one of the pressing issues of introducing modern technologies into the chemical and oil and gas industries. Particularly important are the issues of creating medicines, polymeric materials, remedies for pests and plant diseases, growth stimulants, cornice-forming and coloring substances with unique properties based on fine organic synthesis products. Such compounds include both simple and vinyl esters obtained by vinylation with acetylene of compounds containing hydroxyl, carboxyl, and amino groups in their molecules.

Literature review. According to an analysis of the results of scientific research conducted in recent years throughout the world in the field of organic chemistry, by synthesizing compounds in which the vinyl group is preserved in the molecule, various substances with high physiological activity are synthesized. In this regard, in our republic, the research work of T.S. Sirlibaev, A.G. Makhsumov, S.E. Nurmonov, O.E. Ziyadullaev, E. Turgunov and other scientists has important practical significance [1-3].

Vinyl derivatives are widely used in the field of organic synthesis due to their chemical activity and universal reactivity. Vinyl esters are synthesized in different ways. In particular, the synthesis of simple and vinyl esters by vinylation of compounds containing hydroxyl and carboxyl groups - alcohols, carboxylic acids, hydroxy acids with acetylene - has been well studied. The synthesis of vinyl ethers in an alkaline medium by the Favorsky-Shostakovsky method is especially widely used.

The preparation of vinyl derivatives by migration of the hydrogen atom of the hydroxyl group to the triplet in acetylene and its homologues is one of the common methods of organic synthesis. The use of the superbasic environment in this method is an important factor in increasing the performance of the product [2-7].

While the vinylation of alcohols, acids, and hydroxy acids with acetylene has been studied relatively thoroughly, the vinylation of mono-, di-, and triethanolamines has not been sufficiently analyzed.

Research methodology. This is explained by the presence of two different functional groups in the monoethanolamine molecule, namely an amino group and a hydroxyl group. Therefore, in order to preliminary determine the course of Vinylation reactions, using the Chem 3D Ultra 10.0 program, the spatial structure of the molecules of vinyl ether monoethanolamine, acetylene and Monoethanolamine and the distribution of atomic charges in these molecules were theoretically calculated (Fig. 1-3).

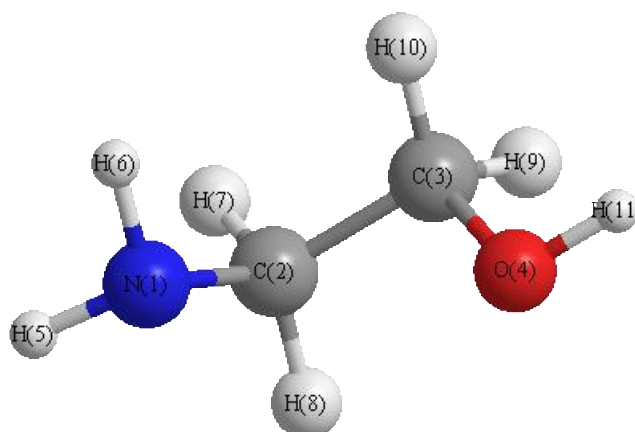


Figure 1. Spatial structure and charge distribution of the monoethanolamine molecule.

Here, -0.284 [N(1)]; 0.031 [C(2)]; 0.151 [C(3)]; -0.374 [O(4)]; 0.110 [H(5)]; 0.110 [H(6)]; 0.009 [H(7)]; 0.024 [H(8)]; 0.012 [H(9)]; 0.012 [H(10)]; 0.199 [H(11)].

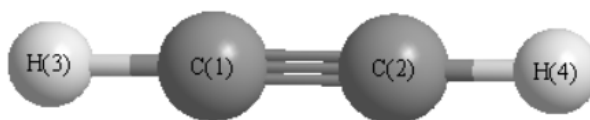


Figure 2. Spatial structure and charge distribution of the acetylene molecule.

Here, -0.53 [C(1)]; -0.53 [C(2)]; 0.53 [H(3)]; 0.53 [H(4)].

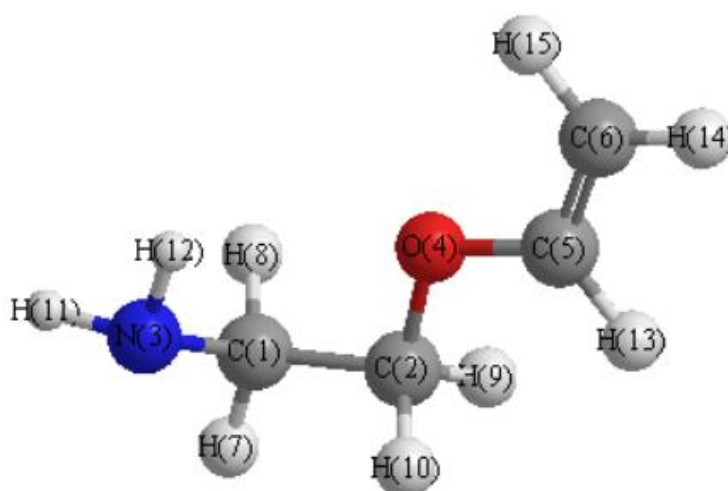


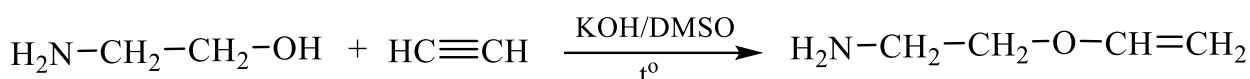
Figure 3. Spatial structure and charge distribution of the monoethanolamine vinyl ether molecule.

Here, 0.030 [C(1)]; 0.152 [C(2)]; -0.285 [N(3)]; -0.163 [O(4)]; 0.221 [C(5)]; -0.327 [C(6)]; 0.025 [H(7)]; 0.007 [H(8)]; 0.012 [H(9)]; 0.013 [H(10)]; 0.110 [H(11)], 0.111 [H(12)], 0.014 [H(13)], 0.040 [H(14)], 0.041 [H(15)].

Apparently, the oxygen atom o (4) (-0.374 EV) in the hydroxyl group of monoethanolamine exhibits a greater nucleophilic property of the molecule. However, the electrophilicity of the hydroxyl group proton in the H(11) molecule (0.199 eV) is higher than that of other protons. This, in turn, determines the direction of the vinyl group towards the hydroxyl group and its replacement with hydrogen.

Analysis of the results. Based on theoretical quantum chemical calculations, it was considered that o-vinyl ether of monoethanolamine (2-(vinylxy)ethanamine) can be formed by vinylation of monoethanolamine and acetylene in the presence of a superbasic medium KOH/DMSO.

The process of vinylation of monoethanolamine with acetylene is carried out according to the following scheme.



In this work, the influence of various factors on the vinylation of monoethanolamine in the presence of acetylene in a KOH/DMSO environment was studied, and the optimal process conditions were determined. During the study, experiments were carried out at an acetylene pressure of 4 atm. The effect of temperature and time on the vinylation reaction in the presence of 20% KOH catalyst relative to the weight of monoethanolamine was studied. The results obtained are shown in Table 1.

Table 1.

The influence of temperature and reaction duration on the reaction of monoethanolamine with acetylene (con catalyst content 20% relative to the mass of monoethanolamine)

Temperature, °C	Reaction duration, hour	Product yield, %
70	3	19,3
70	5	26,3
75	3	26,1
75	5	34,6
80	3	34,4
80	5	38,3
85	3	43,5
85	5	49,7
90	3	49,2
90	5	53,5
95	3	49,3
95	5	50,2

The results show that temperature has a significant effect on the yield of monoethanolamine vinyl ether. The product yield increases with increasing temperature from 19.3 to 53.5%. A further increase in temperature negatively affects

the yield of the product. For example, at 95 °C its yield is 51.5%. This condition is explained by a decrease in the solubility of acetylene in the solvent at very high temperatures, as a result of which its concentration decreases, the reaction rate and the yield of the resulting product decrease. In addition, at high temperatures, the formation of resinous oligomeric substances with vinyl ethers of dimethyl sulfoxide and other reaction intermediates is observed.

Conclusions. In the research work, through theoretical quantum chemical calculations of the starting substances, it was established that the most active reaction center of monoethanolamine is the oxygen atom in its hydroxyl group, the vinyl group formed from acetylene is exchanged for the hydrogen atom of this hydroxyl group. In accordance with theoretical calculations, when vinylating monoethanolamine with acetylene in the presence of a Kon catalyst and a DMSO solvent at a temperature of 70-100 °C and a pressure of 4 atm for 3-5 hours, o-vinyl ether of monoethanolamine - 2-(vinylloxy)ethanamine - is obtained. In this case, the reaction temperature of 95 °C and the reaction duration of 5 hours were chosen as the most favorable conditions.

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