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Synthesis of vinyl acetate in a liquid phase

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ABSTRACT: The article describes the liquid-phase synthesis of vinyl acetate, depending on the nature of the catalyst, the temperature and the feed rate of acetylene, as well as information on the by-products formed during the liquid-phase vinylation. Quantum-chemical calculations are performed and the reaction centers of the molecules are shown.

KEY WORDS: acetylene, acetic acid, vinyl acetate, liquid phase, honey acetate, zinc acetate, cadmium acetate, iron acetate, bismuth acetate, selective, quantum chemical calculations, 3D structure, charge distribution, electron density, reaction center.

I. INTRODUCTION

Among the oxygen-containing compounds produced by the industry of basic organic synthesis, vinyl acetate (VA) occupies the most important place. Today, vinyl acetate is mainly produced in industry from polyvinyl acetate (PVA). Polyvinyl acetate is an invaluable polymer, widely used in various sectors of the economy. Water-based latex paints, water-soluble emulsions, widely used in construction, are produced in large quantities on the basis of PVA. It is the basis of glue, used in the manufacture of furniture. PVA is an effective means of combating radiation. In the hydrolysis of PVA, polyvinyl alcohol is obtained, which goes to the production of synthetic fiber "vinol" and preparation.

In [1], a method was proposed for obtaining vinyl acetate by reacting acetylene with acetic acid at a temperature of 200–300°C, in the presence of a catalyst of iron acetate, followed by distillation and using a phenol-containing compound as a stabilizer.

Vinyl esters of carboxylic acids are obtained by the reaction of carboxylic acids with acetylene in the gas phase at a temperature of 150–300°C in the presence of mixed salts of Zn containing acidic residues of carboxylic acids and H₃PO₄ or H₂SO₄, and for each acid equivalent of carboxylic acids there is 0.15–6 acid equivalents of mineral acid. It is shown that these catalysts serve much longer than zinc salts of carboxylic acids [2].

II. SIGNIFICANCE OF THE SYSTEM

By acetylation of acetylene according to the technology developed in the polymer laboratory (UAR (UAE), Cairo), a pilot plant for the production of vinyl acetate was constructed. The yield of vinyl acetate in terms of AcOH was 17% [4]. A catalyst prepared by mixing solutions of 32 g of HgO in 150 g of glacial acetic acid and a solution of 6.38 g of BF₃ was used. The resulting insoluble Hg compound was mixed with the ion exchange resin in the hydrogen form (sulfonated copolymer with divinylbenzene) as a cocatalyst. Pre-activated, washed and dried catalyst had a particle size of 120–170 mm.

III. LITERATURE SURVEY

Liquid-phase reaction of acetylene with aliphatic acids at a temperature of 50–300°C (70–200°C) in the presence of oxygen and a catalyst for Pd or its salts and oxyhalides gives aliphatic acid vinyl esters [3].

In [5], the preparation of vinyl esters of carboxylic acids <C₁₈ by the reaction of acetylene with carboxylic acids at atmospheric pressure in the presence of zinc salts of carboxylic acids as a catalyst is described. Zinc salts take in the amount of 4–12% by weight of the liquid phase in which the reaction takes place. To increase their activity, salts of Zn are recommended to add chlorides of Be, Ba, Al, Co and mixtures of rare-earth elements. The starting components are preferably obtained by the reaction of Co with olefin oligomers. C₂–C₄.

Known [6] a catalytic method for the preparation of vinyl ethers by the interaction of carboxylic acids with acetylene in the gas phase. A mixture of carboxylic acids and a diluent at a ratio of 1: 5 in the presence of a polymerization inhibitor (hydroquinone, pyrocatechin, thymol) is passed with acetylene over the catalyst at a temperature of more than 150°C and below the decomposition temperature of the carboxylic acid (CC). The molar ratio of QC: C₂H₂ = 1: 2–30. Aliphatic, cycloaliphatic, alkylaromatic or aromatic hydrocarbons and other substances that are inert under the reaction conditions and form an azeotropic mixture with a carboxylic acid are used as diluents, boiling temperature of which is 400 and below atmospheric pressure and 100°C above the boiling point of the vinyl acid at atmospheric pressure. ester of the corresponding carboxylic acid. V-esters of p-toluic, o-chlorine-benzoic, crotonic, formic and chlorineacetic acids have been synthesized.

IV. METHODOLOGY

A. METHODS OF CONDUCTING EXPERIMENTS.

The reaction was carried out in a bubbler type reactor in the temperature range 60-70°C. Single- and multicomponent systems based on cadmium, zinc, copper, and iron, as well as bismuth, were used as catalysts. Vinyl acetate as it was formed was removed from the reaction zone in the form of vapor extracted by excess acetylene. They were condensed in a refrigerator in a trap and sent for rectification, and acetylene separated from the liquid was returned to the system. The effect of catalyst composition on the yield of vinyl acetate and the productivity of the process (Table 1) was studied.

Table 1

The influence of the composition of the catalyst on the yield of vinyl acetate and the productivity of the process (T = 65-70°C, VC₂H₂- 75 l / 1 CH₃COOH * hour). The amount of catalyst 5% by weight of acetic acid

| № | Catalyst composition, % | Process performance, g/l catalytic hour | The output of vinyl acetate on the reacted acetylene, % | Acetylene conversion, % |
|---|--|---|---|-------------------------|
| 1 | Cu(CH ₃ COO) ₂ | 120,0 | 65,0 | 85.0 |
| 2 | Cd(CH ₃ COO) ₂ | 115,3 | 58,0 | 83.0 |
| 3 | Zn(CH ₃ COO) ₂ | 100,0 | 53,0 | 75.0 |
| 4 | Fe(CH ₃ COO) ₂ | 45,0 | 29,0 | 70.0 |
| 5 | Cu(CH ₃ COO) ₂ : Cd(CH ₃ COO) ₂ =1:1 | 132,0 | 67,0 | 86.0 |
| 6 | Zn(CH ₃ COO) ₂ -70,0 Cd(CH ₃ COO) ₂ -30,0 | 82,0 | 72,0 | 81,0 |
| 7 | Zn(CH ₃ COO) ₂ -70,0 Cd(CH ₃ COO) ₂ -20,0 Cu(CH ₃ COO) ₂ -10,0 | 95,0 | 82,0 | 84,0 |
| 8 | Zn(CH ₃ COO) ₂ -70,0 Cd(CH ₃ COO) ₂ -20,0 Bi(CH ₃ COO) ₃ 10,0 | 110,0 | 88,0 | 92,0 |

The table shows that the highest yield of vinyl acetate and the productivity of the process occur when using two- and three-component systems (catalysts No. 5 - 8). Among single-component systems, copper acetate exhibits the greatest activity, since copper ions form active complexes with acetylene.

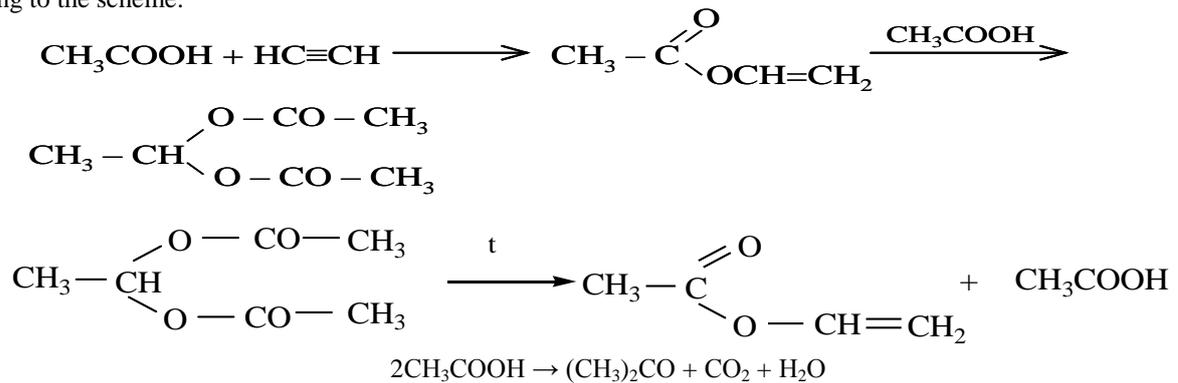
It was established that the selectivity of the process mainly depends on the feed rate of acetylene (Table 2).

Table 2

The dependence of the selectivity of the process on the feed rate of acetylene. The catalyst Cu (CH₃COO) 2–5% by weight of acetic acid. T=70⁰C, VCH₃COOH-500cm³

| № | Acetylene feed rate, l/h | The composition of catalyzate, % weight | | |
|----|--------------------------|---|----------------------|---------------|
| | | Vinyl acetate | Ethylidene diacetate | Σ by-products |
| 1. | 50 | 15,0 | 82,0 | 3,0 |
| 2. | 75 | 65,0 | 32,0 | 3,0 |
| 2. | 100 | 70,0 | 26,0 | 4,0 |
| 3. | 150 | 75,0 | 21,0 | 4,0 |
| 4. | 200 | 84,0 | 15,0 | 1,0 |
| 5. | 250 | 95,0 | 3,0 | 2,0 |
| 6. | 300,0 | 96,0 | 3,5 | 0,5 |

It has been proven that with an increase in the acetylene feed rate, the content of vinyl acetate in the reaction products increases. However, carrying out the process at high feed rates of acetylene is associated with certain difficulties. On this basis, the process was then carried out at an acetylene flow rate of 100-150 l / h⁻¹ (70-75 l/h. CH₃COOH hour). As a by-product in the liquid-phase vinylation, ethylidene diacetate and acetone are formed according to the scheme:



The formation of ethylidene diacetate was proven as follows. The catalyst was passed through a bed of Goody's aluminosilicate catalyst at 280-420⁰C with a bulk velocity of 0.4-0.6 l*h⁻¹. It was established that with increasing temperature, the degree of decomposition of ethylidene diacetate increases (Table 3). To prove this, the counter synthesis was carried out: acetic acid was passed through a catalyst bed at 200–420⁰C, acetone was obtained with a yield of 85.0–90.0%. The detection of 1-4% water in products confirms this again.

Table 3

Dependence of the degree of decomposition of ethylidene diacetate on temperature

| № | Temperature, ⁰ C | The composition of catalyzate, % weight. | | | |
|----|-----------------------------|--|---------------|-------------|---------|
| | | Ethylidene diacetate | Vinyl acetate | Acetic acid | Acetone |
| 1. | 280 | 32 | 42,0 | 26,0 | - |
| 2. | 300 | 28 | 50,0 | 22,0 | - |
| 3. | 320 | 21,0 | 59,0 | 18,0 | 2,0 |
| 4. | 330 | 14,0 | 72,0 | 8,0 | 6,0 |
| 5. | 360 | 8,0 | 80,0 | 2,0 | 10,0 |
| 6. | 380 | 6,0 | 80,0 | 2,0 | 12 |
| 7. | 400 | 3,0 | 80,0 | 1,0 | 16,0 |
| 8. | 420 | insignificantly | 80,0 | - | 20,0 |

It is proved that at 280°C the yield of ethylidene diacetate in the composition of catalyzate is 32%, and at 420°C only traces remain, at the same time an increase in the yield of vinyl acetate from 42.0% (at 280°C) to 80.0% (at 420°C) and an increase in the formation of acetone from 2.0% (at 320°C) up to 20.0% (at 420°C).

The effect of acetylene space velocity and temperature on the yield of vinyl acetate was studied (Tables 4 and 5).

Table 4

The effect of acetylene flow rate on process selectivity,

T = 70 - 80°C. The composition of the catalyst Zn (CH₃COO)₂ -70%, Cd (CH₃COO)₂-20%, Cu (CH₃COO)₂-10%, and the amount of its 2.0%

| Acetylene flow rate, l·h ⁻¹ | The composition of catalyzate, % | | |
|--|----------------------------------|---------------|----------------------|
| | Acetone | Vinyl acetate | Ethylidene diacetate |
| 50 | 5,0 | 55,0 | 40,0 |
| 75 | 7,0 | 82,0 | 11,0 |
| 100 | 8,0 | 83,0 | 9,0 |
| 150 | 6,0 | 85,0 | 9,0 |
| 200 | 5,0 | 88,0 | 7,0 |
| 250 | 6,0 | 79,0 | 8,0 |

The table shows that with an increase in the flow rate of acetylene, the selectivity of the formation of vinyl acetate gradually increases. At low volumetric rates, acetic acid is probably added to the vinyl acetate to form ethylidene diacetate..

Table 5

The effect of temperature on the selectivity of the formation of vinyl acetate Catalyst: Zn(CH₃COO)₂ -70%, Cd(CH₃COO)₂-20%, Cu(CH₃COO)₂-10%, VC₂H₂ -75 l·h⁻¹

| Temperature, °C | The composition of catalyzate, % | | |
|-----------------|----------------------------------|---------------|----------------------|
| | Acetone | Vinyl acetate | Ethylidene diacetate |
| 70 | 5,0 | 82,0 | 6,0 |
| 80 | 7,0 | 85,0 | 8,0 |
| 90 | 10,0 | 82,0 | 8,0 |
| 100 | 14,0 | 75,0 | 11,0 |
| 110 | 17,0 | 65,0 | 18,0 |
| 120 | 20,0 | 60,0 | 20,0 |

It has been established that with increasing temperature, the content of acetone and ethylidene diacetate in catalyzate gradually increases.

V. EXPERIMENTAL RESULTS

The result of applying the methods of quantum chemistry is information about the density of electronic states, the distribution of electron density, potential reaction surfaces and calculations of various spectroscopic quantities. Currently, quantum chemistry methods are cheaper, affordable, and universal methods for studying the electronic structure of molecules. However, it is necessary to understand that, nevertheless, it is impossible to completely abandon the expensive experimental methods for the study of matter.

The activity of a molecule in any reactions mainly depends on its structure and energy characteristics. Prediction of the reactivity of organic molecules is a very difficult and urgent task. With the development of quantum chemical calculation methods, chemists have acquired the ability to plan experimental studies and conduct directional synthesis of target products.

In this paper, the 3D structures, charge distribution and electron density of acetylene, acetic acid and vinyl acetate were investigated by the widely used Hyper Chem. program using the semi-empirical quantum-chemical method of RMZ.

As an example, we present the results of studying the geometry and electronic structure of acetylene, acetic acid and vinyl acetate molecules.

Figure 1 shows the 3D structure of vinyl acetate. It was shown that instead of hydrogen, the hydroxyl group replaces the vinyl group, which has carbons in the sp^2 hybrid state.

Also shown are the charge and electron density distributions over the atoms in the acetylene molecule, acetic acid, and vinyl acetate (Figure 2 and Figure 3). Comparison of the values of electron charges of the selected molecules showed that the greatest amount of negative charge in the vinyl acetate molecule is concentrated on the oxygen atom. Most likely, because of this, the oxygen atom is the reaction center, through which the catalytic vinylation reaction is carried out with acetylene.

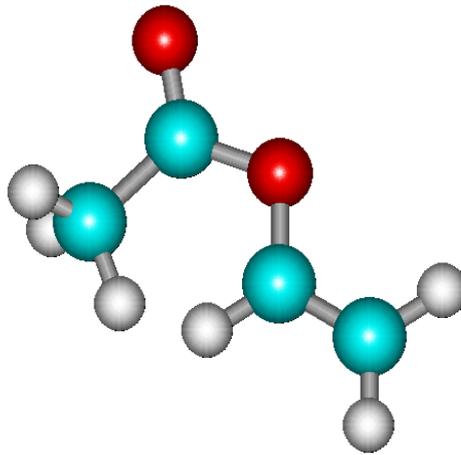


Fig.1. 3D structure of vinyl acetate

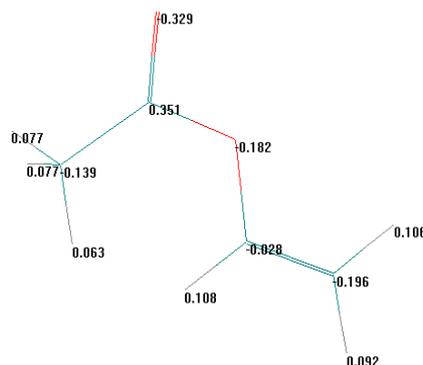


Fig.2. Charge distribution in vinyl acetate molecule

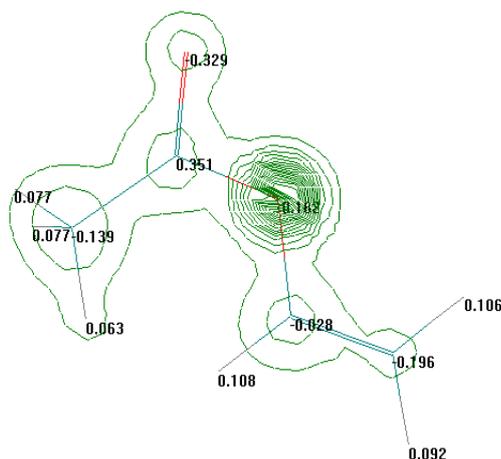


Fig.3. The distribution of electron density by atoms in the molecule of vinyl acetate

We also carried out quantum chemical calculations (total energy, formation energy, heat of formation, electron energy, nuclear energy, dipole moment, oxygen atom charge), the results of which are shown in Table 6.

Table 6

Quantum-chemical calculations of the studied compounds

| Nature of the compound | Total energy, kcal / mol | Energy of education, kcal / mol | Heat of formation, kcal / mol | Electron energy, eV | Nuclear energy, kcal / mol | Dipole moment (D) | Oxygen charge |
|------------------------------|--------------------------|---------------------------------|-------------------------------|---------------------|----------------------------|-------------------|---------------|
| Raw materials | | | | | | | |
| Acetylene | -6489,10351 | -391,2214355 | 54,76256943 | -12975,6523 | 6486,5493 16 | 0,0172 8 | - |
| Acetic acid | - 20449,64063 | -768,5530396 | - 99,24705505 | - 56742,63281 | 36292,992 19 | 4,234 | -0,271 |
| Synthesized compounds | | | | | | | |
| Synthesized compounds | - 26579,79883 | -1183,608521 | - 68,31852722 | - 93369.19531 | 66771,398 84 | 4,004 | -0,182 |

VI. CONCLUSION AND FUTURE WORK

Thus, the influence of the acetylene space velocity and temperature on the selectivity of the formation of vinyl acetate in the presence of a catalyst of composition Zn (CH₃COO)₂ -70%, Cd(CH₃COO)₂-20%, Cu(CH₃COO)₂-10% and Cu(CH₃COO)₂-100%. Some regularities of the process are defined.

Chemistry has traditionally been and remains an experimental science. In modern computer chemistry, using various programs based on the results of quantum-chemical and molecular-dynamic calculations, one can assume in advance about the properties of a molecule. Nevertheless, quantum-chemical and, especially, molecular-dynamic calculations have not yet received due distribution in our republic.

Compounds of acetylene, acetic acid, and vinyl acetate have been studied. Thus, based on the results of studying the structure, charge distribution, electron density, and energy characteristics of selected molecules by semi-empirical quantum-chemical methods, the reaction centers of the molecules used have been identified, which in turn are used to specifically coordinate the studied reaction components.



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