HETEROGENEOUS CATALYTIC VINYLATION REACTION OF CYANURIC ACID WITH THE PARTICIPATION OF ACETYLENE AND VARIOUS CATALYSTS

Abstract: The work describes the processes of synthesis of cyanuric acid, its mono-, di-, tri-vinyl ethers in the solvent, C_{act}/KOH system under pressure, optimal synthesis conditions, catalyst activation, the effect of the molar ratio of the starting materials on the yield of cyanuric acid vinyl ethers, analyzed the effect of structure and the number of radicals in the structure of vinyl esters of cyanuric acid during the process, data of chromatography-mass spectroscopic analysis are presented.

Key words*: cyanuric acid, acetylene, vinylation, catalyst, catalytic reaction, mono-vinyl ether, di-vinyl ether, tri-vinyl ether.*

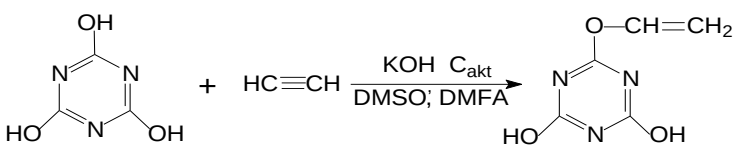
Introduction. On the basis of heterocyclic compounds containing nitrogen, substances with a vinyl group are obtained in the world, which are used as polymers, insecticides, drugs, sorbents, biologically active substances and composite materials used in medicine, agriculture, chemical industry, textile, paint and varnish, perfumery industry [1].

Another characteristic feature of cyanuric acid is the active hydrogen atom in its composition, which plays an important role in the formation of Hamilton complexes [2-3]. The synthesis of vinyl compounds 2,4,6-trihydroxy 1,3,5-triazine was initially carried out with the participation of acetylene at atmospheric pressure by catalytic vinylation in a system with a high content of bases due to the active hydrogen atom in the molecule and the corresponding vinyl esters were synthesized. the yield of the product formed during the reaction and the optimal parameters were determined [4-5]. The reactions of the addition of a number of compounds containing a hydroxyl group in their molecule with acetylene have been studied, and the role of heterogeneous catalysts in this is very important. In heterogeneous catalytic processes, catalysts are mostly solid, while the starting materials are mainly in a gaseous (vapor) state [6-7].

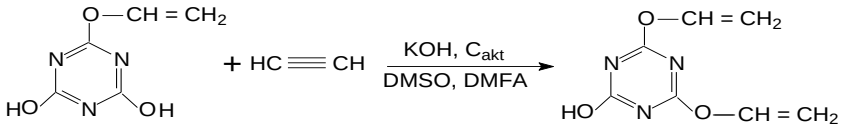
Methods and materials. The vinylation reaction of cyanuric acid was carried out homogeneously by the catalytic method in a reactor of the RSG 1.6-100 / 6 K1 type at a pressure of 10 atm. at different temperatures and duration of reaction with acetylene. In this case, the vinylating agent is acetylene (from a balloon); KOH / C_{act} and the solvent DMSO were used as a catalyst. The resulting catalysate was extracted with diethyl ether, the solvent was distilled off from the organic portion, and the residue was fractionated in vacuo.

The obtained substances were analyzed by IR-, ^{1}H, ^{13}C-NMR [8-10], using methods using a gas chromatography-mass spectrometer APCI Method from Agilent Technologies 6420 in a column with 5% phenylmethyl-silicone liquid CI 18, in the temperature range from 150^0C to 320^0C with inert mass spectrum of Agilent Technologies 9973 with control parameter up to 500^0C.

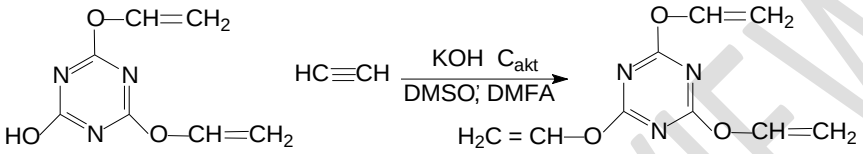
Results and discussion: The study considered the synthesis of cyanuric acid vinyl esters by the heterogeneous catalytic method. In the reaction, (solvent + KOH/C_{act}) is used as a catalyst. The reaction scheme of the process is as follows:



In the process, it was determined that mono-, di- and trivinyl esters of cyanuric acid are formed depending on the conditions (molar ratio of the starting materials, their feed rate, temperature):



By adding acetylene to di-vinyl ether and by increasing the reaction time, trivinyl acid ester was synthesized:



In the reaction of vinylation of cyanuric acid by a heterogeneous method, the effect of temperature and molar ratio of the starting products on the product yield was studied. Catalysts used in heterogeneous catalytic reactions cannot fully manifest their catalytic activity at the very beginning of the reaction. A certain adaptation of the catalyst to the process is required. Therefore, it takes time to establish a stable (constant) value of the product yield in the process. Therefore, the time of transition of the catalyst to the active state was initially determined (Table 1).

Table 1

Determination of the catalyst transition time to the active state (C_{act}/KOH, temperature 350 ^{0}C, molar ratio of acetylene-cyanuric acid 1:1)

Process duration, hour	Cyanuric acid vinyl esters yield,%
1	10,2
2	25,4
3	42,6
4	56,5
5	60,4
6	61,2
7	61,4
8	61,5
9	61,5
10	61,5

The process was carried out for 10 hours at a temperature of 350 ^{0}C. The molar ratio of the starting materials is 1:1, the rate of acetylene is 1 L/h, the weight of the catalyst is 100 g, and the weight of cyanuric acid is 5.76 g.

The analysis of the obtained results shows that in the first 5 hours the product yield increases sharply, for 1 hour the yield of vinyl esters was 10.2 %, for 7 hours - 61.4 %. And in the following hours, the product yield did not change. This means that in the process of vinylation of cyanuric acid, it takes 7 hours for the catalyst (KOH/C_{act}) to work in an active stationary state. During this time, it can be said that the catalyst is texturally positioned relative to the reaction of acetylene and cyanuric acid.

Heterogeneous catalytic reactions proceed at a slightly higher temperature than homogeneous catalytic reactions, and the temperature range is also carried out in a wide range. Therefore, the effect

of temperature on the yield of the reaction products of the vinylation of cyanuric acid with acetylene was investigated by the heterogeneous catalytic method (Table 2).

Table 2

Effect of temperature on the yield of the reaction products of vinylation of cyanuric acid with acetylene by the heterogeneous method

№	Reaction temperature, ^{o}C	Yield of vinyl esters of cyanuric acid, %
1	380	75,5
2	400	81,3
3	420	90,8
4	440	82,4
5	460	78,6
6	480	72,0

It was determined that the change in temperature affects the yield of vinyl cyanuric acid esters. As a result of the process taking place in the temperature range of 380-420 ^{0}C, the yield increased from 69.2 % to 90.8 %, respectively. A further increase in temperature leads to a decrease in the yield of the reaction products. At 440 and 480 ^{0}C, the yield of vinyl esters was 82.4 % and 72.0 %, respectively. Thus, the optimum temperature for synthesizing vinyl esters under these conditions is 420 ^{0}C.

This can be explained by the adsorption processes that occur during heterogeneous catalysis. In heterogeneous catalytic reactions, the ratio of the moles of the starting materials and the rate of their release are also of great importance. Therefore, the study studied the effect of the molar ratios of acetylene and cyanuric acid on the yield of vinyl esters in a heterogeneous system (Table 3).

Table 3

Influence of the molar ratio of the starting materials on the yield of vinyl esters of cyanuric acid (amount of cyanuric acid 0.045 mol/h temperature 420 ^{0}C)

Molar ratio Acetylene: C.A.	The output of vinyl esters of cyanuric acid mass ./%			
	Monovinyl ether	Divinyl ether	Trivinyl ether	General
1:1	86	10	4	66,6
2:1	63	24	13	71,5
3:1	52	30	18	82,7
4:1	43	35	22	86,4
5:1	37	36	27	86,8
1:2	87	11	2	57,3
1:3	92	7	1	52,6
1:4	95	5	-	50,8
1:5	95	5	-	41,4

In the reaction of acetylene and cyanuric acid, cyanuric acid is active. When taken in equimolar proportions, the overall vinyl ester yield (compared to cyanuric acid) was 66.6%. 86 wt ./% of this product corresponds to monovinyl ether, 10 mass./% di- and 4 mass./% di and trivinyl ether.

With an increase in the amount of acetylene in the ratio of moles of primary substances, the total yield of vinyl esters increases. For example, the molar ratio of acetylene: cyanuric acid varies from 1:1 to 1:5, the yield of vinyl esters is increased from 66.6 % to 86.8, while the yield of monovinyl esters is reduced from 86 to 37 mass/%. Conversely, a change in the ratio of moles of acetylene:

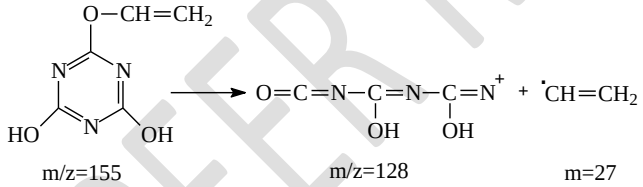
cyanuric acid from 1: 1 to 5: 1 reduces the yield of esters from 66.6 % to 41.4, while the yield of monovinyl esters increases from 86 to 95 mass/%. In all cases, a mixture of mono-, di- and trivinyl ethers is obtained.

Among vinyl ethers, monovinyl ether is the main one in terms of yield. An increase in the yield of monovinyl ether leads to a decrease in the yield of di- and trivinyl ethers.

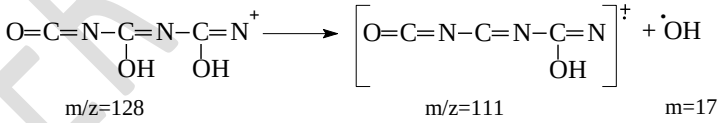
Based on the results obtained, it can be said that the reaction of vinylation of cyanuric acid with acetylene in the presence of a catalyst (KOH / C_{act}.), By a heterogeneous method, forms mono-, di- and trivinyl esters of cyanuric acid. The maximum value of their total output was reached up to 86.8. The maximum yield of mono-, di- and trivinyl ethers is 95; 36 and 27 mass./%. respectively.

Chromate-mass spectroscopic analysis of the synthesized substances. In the chromatography-mass spectrum of the synthesized mono-vinyl ester of cyanuric acid (2,4-dihydroxy-6- (vinyloxy) -1,3,5-triazine), the formation of ions corresponding to their molecular weight and the mass of fractional ions formed during their decomposition was determined ... The peak of the ion separated from the 2,4-dihydroxy-6- (vinyloxy) -1,3,5-triazine molecule was 154.9. Below is a chromatography-mass spectral analysis of fractional ions formed from the parent molecular ion. In addition, it was determined from the spectrum that fractional ions with masses m\z 128.1, m\z 111, m\z 85, m\z 46 and m\z 16.1 are formed.

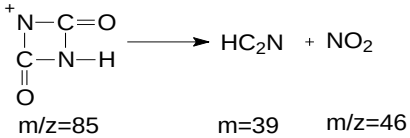
After the introduction of 2,4-dihydroxy-6- (vinyloxy) -1,3,5-triazine into the gas chromatography-mass spectrometer, under the chosen conditions, as a result of the release of the vinyl radical in 0.712 minutes, an isocyanatformamide acid ion with m\z 128 was formed.



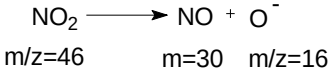
In turn, a hydroxo radical is released in one direction from the isocyanate formimide ion in 0.175 minutes, the molecular ion of 1- (isocyanate methylene) isourea with m\z 111 decomposes.



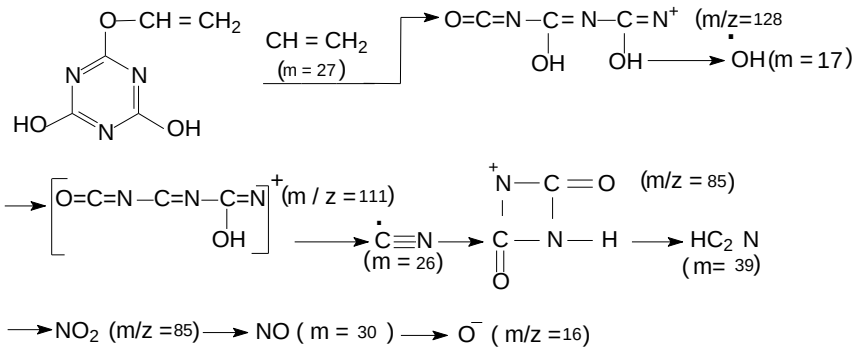
Likewise, the isolation of the molecular ion HC_2N from the composition of the 1,3-diazetidine-2,4-diol ion forms nitric oxide (IV).



Nitrogen oxide (IV) decays, forms an oxygen ion with m/z 16:

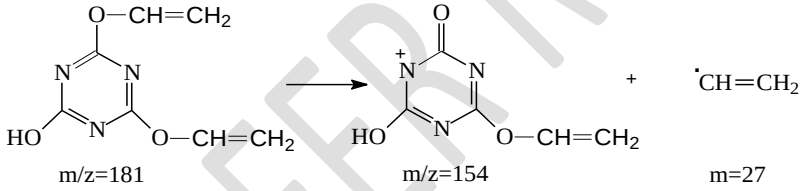


The decomposition of 2,4-dihydrosy-6- (vinyloxy) -1,3,5-triazine into fractional ions in the chromatography-mass spectrum can be depicted in general form as follows:

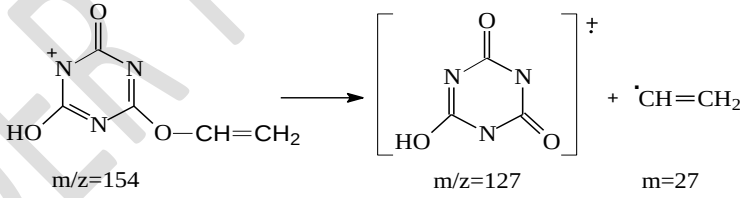


In the chromatography-mass spectrum of the synthesized cyanuric acid divinyl ester (2-hydroxy-4,6-bitz (vinyloxy) -1,3,5-triazine), the formation of ions corresponding to their molecular weight and the mass of the formed fractional ions was determined. In this case, the peak of the ion separated from the molecule of 2-hydroxy-4,6-bits (vinyloxy) - 1,3,5-triazine was equal to 180.9. Below is a chromatography-mass spectrum of fractional ions formed from the parent molecular ion. In addition, fractional ions with a mass m\z 154.9 are formed in the spectrum; m\z 127.1; m\z 85.1; m\z 46 and m\z 16.1.

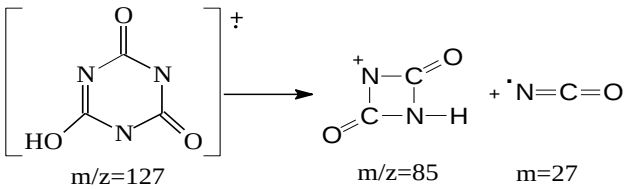
After 2-hydroxy-4,6-bitz (vinyloxy) -1,3,5-triazine was introduced into the gas chromatography-mass spectrometer, under the selected conditions in 0.712 minutes by separation of the vinyl radical, the 2-hydroxy-4 , 6-bits (vinyloxy) - 1,3,5-triazine with m\z 154.



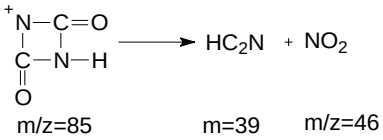
In turn, a vinyl radical is separated in one direction from 2-hydroxy-4,6-bits (vinyloxy) -1,3,5-triazine in 0.175 minutes and the 6-hydroxy-1,3,5-triazine-2 ion is formed , 4-diol with m\z 127.



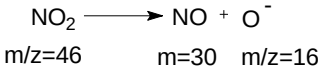
In a chromatography-mass spectrum, fractional ions formed from a molecular ion also form small ionic fragments. As a result of the separation of the N = C = O radical from the 6-hydroxy-1,3,5-triazine-2,4-diol ion, an ion with m\z 85 is formed.



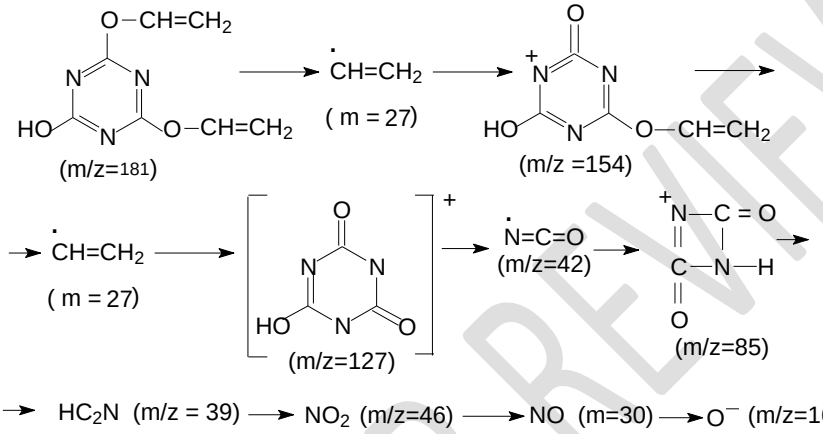
Likewise, nitric oxide (IV) is formed by the separation of the HC_2N molecular ion from 1,3-diazetidine-2,4-diol.



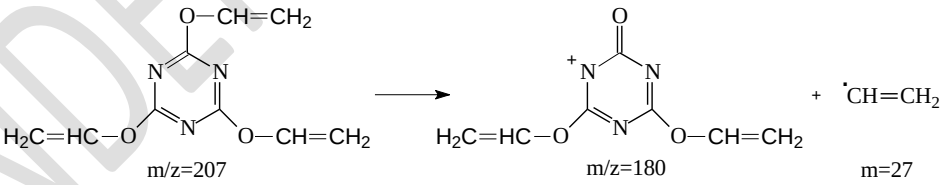
Nitric oxide (IV) decomposes to nitric oxide (II) and an oxygen ion with m / z 16 is formed.



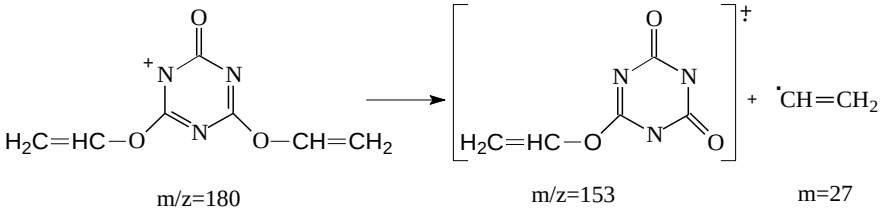
The decomposition into fractional ions of 2,4-hydroxy-6- (vinyloxy) -1,3,5-triazine in the chromatography-mass spectrum can be depicted as follows:



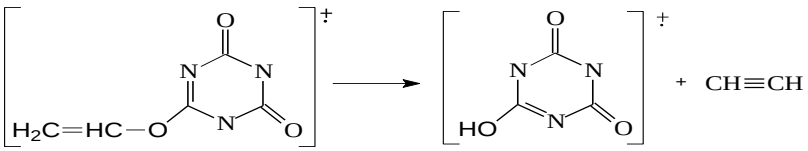
In the chromatography-mass spectrum of cyanuric acid trivinyl ester (2,4,6-tris- (vinyloxy) -1,3,5-triazine), the formation of ions corresponding to their molecular mass and the mass of fractional ions formed during their decomposition was determined. In this case, the peak of the ion separated from the 2,4,6-tris- (vinyloxy) - 1,3,5-triazine molecule is equal to 180. The chromatography-mass spectrum of fractional ions formed from the initial molecular ion is shown below. In addition, fractional ions with m\z 153 are formed in the spectrum; m\z 127.1; m\z 85.1; m\z 46 and m\z 16. After the introduction of 2,4,6-tric- (vinyloxy) -1,3,5-triazine into the chromatography-mass spectrum, under the selected conditions in 0.712 minutes the vinyl radical is separated and an ion is formed 2-hydroxy-4,6-bit- (vinyloxy) -1,3,5-triazine with m\z 180.



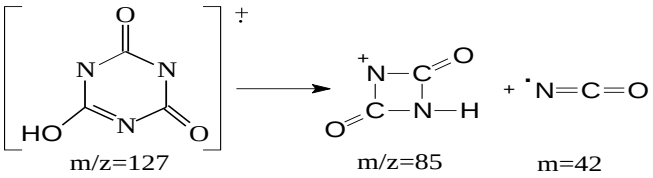
In turn, from the ion of 2-hydroxy-4,6-bit- (vinyloxy) -1,3,5-triazine in 0.175 minutes, from the decomposition of the radical vinyl fraction in one direction, an ion of 2,4-hydroxy-6- (vinyloxy) -1,3,5-triazine with m\z 153.



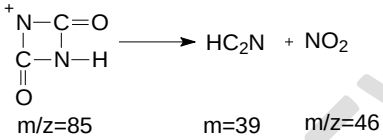
As a result of the separation of the molecular ion of acetylene from 2,4-hydroxy-6- (methylvinyl) -1,3,5-triazine, the formation of an ion with m\z 127 was observed.



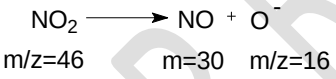
As a result of the separation of the .N = C = O radical from 2,4-hydroxy-6- (vinyloxy) -1,3,5-triazine, 1,3-diazetidine-2,4-dione is formed.



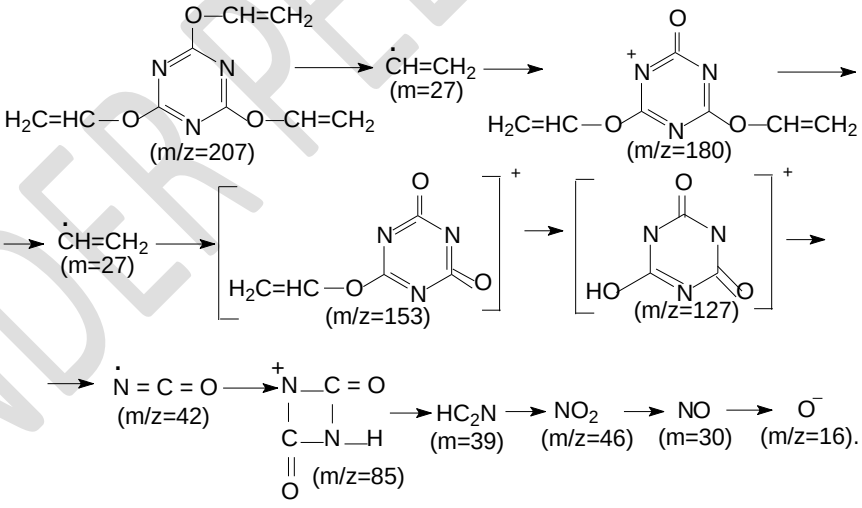
In turn, 1,3-diazetidine-2,4-diol decomposes with the release of the molecular ion HC_2N and nitric oxide (IV) with m/z 46 is formed.



The spectrum contains an oxygen ion, which is formed as a result of the decomposition of nitrogen oxide (IV).



In the chromate-mass spectrum of 2,4,6-tric- (vinyloxy) -1,3,5-triazine, the direction of decomposition into ions can be expressed as follows:



Conclusions: The process of vinylation of cyanuric acid was carried out by a heterogeneous catalytic method with the participation of KOH under pressure, activated carbon and solvents, and vinyl esters were synthesized, a reaction mechanism was proposed, the amount of catalyst and optimal solvents, as well as the optimal process parameters, were determined. The structure of the synthesized compounds was proved using the methods of ^{1}H-, ^{13}C-spectroscopy and gas chromatography-mass spectrometry, and it was proved that the high electron density in the hydrogen atom of the hydroxyl group is a reaction center that allows the vinylation process to proceed.

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