Current Journal of Applied Science and Technology

41(1): 14-22, 2022; Article no.CJAST.80796
ISSN: 2457-1024
(Past name: British Journal of Applied Science & Technology, Past ISSN: 2231-0843, NLM ID: 101664541)

Heterogeneous Catalytic Vinylation Reaction of Cyanuric Acid with the Participation of Acetylene and Various Catalysts

A. E. Ziyadullaev [a*], S. E. Nurmanov [b] and N. F. Davronova [c]

[a] Tashkent Institute of Chemical Technology, Uzbekistan.
[b] National University of Uzbekistan, Uzbekistan.
[c] Tashkent State Pedagogical University, Uzbekistan.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CJAST/2022/v41i131644

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/80796

Original Research Article

Received 04 November 2021
Accepted 08 January 2022
Published 12 January 2022

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. It is known that cyanuric acid and its halogenated derivatives are used as biologically active substances. Analysis of the results shows that cyanuric acid can kill 72% of the studied microorganisms. Replacing the hydroxyl group in the cyanuric acid molecule with a vinyl group increases the biological activity of the compound, as well as its resistance to microorganisms.

Keywords: Cyanuric acid; acetylene; vinylation; catalyst; catalytic reaction; mono-vinyl ether; di-vinyl ether; tri-vinyl ether.

1. INTRODUCTION

Today, in the world, the synthesis of new types of organic substances in the chemical industry, the synthesis of compounds with different properties on their basis and the study of their properties is an urgent task. Therefore, the synthesis of vinyl esters in the presence of catalysts and organic

**Corresponding author: E-mail: anvar_ziyadullayev@mail.ru;*

solvents in the vinylation of heterocyclic compounds containing a hydroxyl group remains one of the urgent problems in organic chemistry. In particular, scientific work is underway to develop methods for producing vinyl compounds based on substances containing an active hydrogen atom in the presence of highly basic systems at atmospheric pressure and catalysts at high pressure.

Another feature of cyanuric acid is the active hydrogen atom, which plays an important role in the formation of Hamilton complexes [1-2]. The formation of these complexes occurs due to the interaction of active hydrogen with substrates containing electron donors. These features make it possible to obtain new compounds from cyanuric acid that can be used in biochemistry and pharmaceutical industry [3-4]. According to D.J. Cram, in many cases the ketone form of substances is more stable than the enol form. But, in heteroatoms located near carbonyl groups, there are unbound electrons, they lead to cyclic delocation and, as a result, aromaticity appears [5-6].

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.

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 [7-9]. 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 [10-12]. 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 [13-14].

It is known that cyanuric acid and its halogenated derivatives are used as biologically active substances. As a result of the introduction of a vinyl group into its molecule, its biological activity is further enhanced. For this reason, the biological activity of vinyl esters of synthesized cyanuric acid was studied.

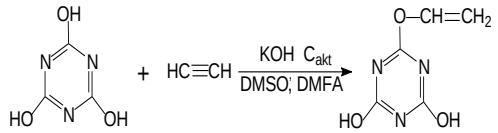
2. METHODS AND MATERIALS

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.

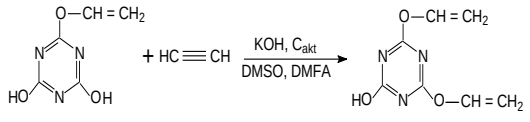
The obtained substances were analyzed by IR-, ^{1}H, ^{13}C-NMR [15-16], using methods using a gas chromatography-mass spectrometer APCI Method from Agilent Technologies 6420 in a column with 5% phenylmethyl-silicone liquid CI 18, in the temperature range from $150^{0}C$ to $320^{0}C$ with inert mass spectrum of Agilent Technologies 9973 with control parameter up to $500^{0}C$.

3. RESULTS AND DISCUSSION

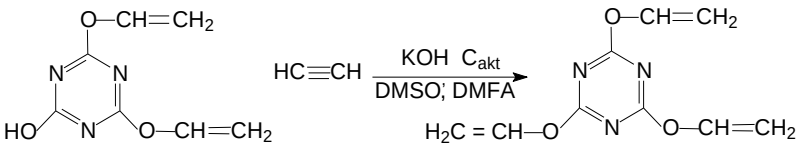
The study considered the synthesis of cyanuric acid vinyl esters by the heterogeneous catalytic method. In the reaction, (solvent + KOH/C_{act}) is used as a catalyst. The reaction scheme of the process is as follows:



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).

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).

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.

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, °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

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)

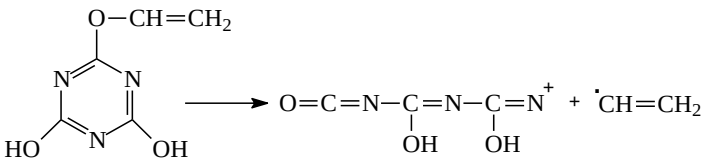
Molar ratio Acetylene: C.A.	The output of vinyl esters of cyanuric acid mass ./%			
	Monovinyl ether	Divinyl ether	Trivinyl ether	General
1:1	86	10	4	66,6
2:1	63	24	13	71,5
3:1	52	30	18	82,7
4:1	43	35	22	86,4
5:1	37	36	27	86,8
1:2	87	11	2	57,3
1:3	92	7	1	52,6
1:4	95	5	-	50,8
1:5	95	5	-	41,4

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.

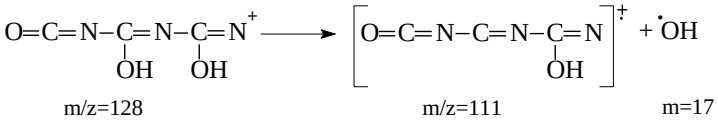
Chromate-mass spectroscopic analysis of the synthesized substances. In the chromatography-mass spectrum of the synthesized mono-vinyl ester of cyanuric acid (2,4-dihydroxy-6- (vinyloxy) - 1,3,5-triazine), the formation of ions corresponding to their molecular weight and the mass of fractional ions formed 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.

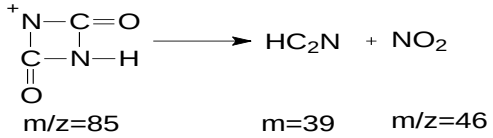


m/z=155 m/z=128 m=27

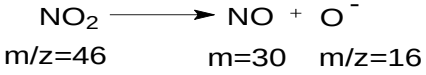
In turn, a hydroxo radical is released in one direction from the isocyanate formimide ion in 0.175 minutes, the molecular ion of 1- (isocyanate methylene) isourea with m\z 111 decomposes.



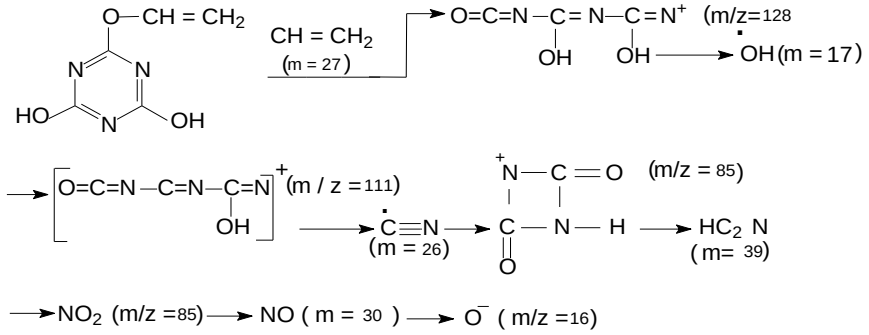
Likewise, the isolation of the molecular ion HC_2N from the composition of the 1,3-diazetidine-2,4-diol ion forms nitric oxide (IV).



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

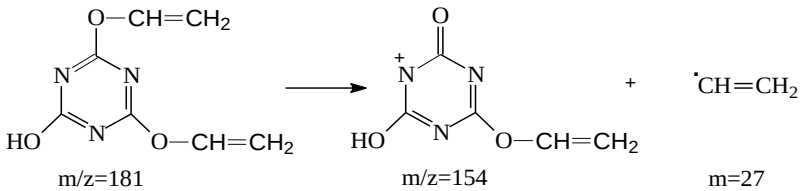


The decomposition of 2,4-dihydrosy-6- (vinyloxy) -1,3,5-triazine into fractional ions in the chromatography-mass spectrum can be depicted in general form as follows:

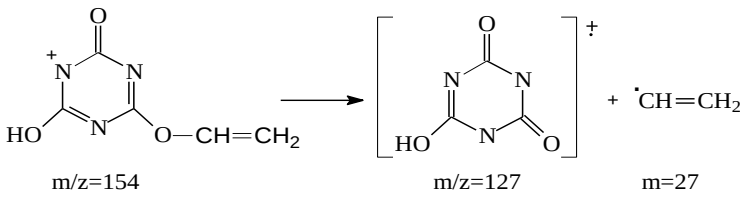


In the chromatography-mass spectrum of the synthesized cyanuric acid divinyl ester (2-hydroxy-4,6-bitz (vinyloxy) -1,3,5-triazine), the formation of ions corresponding to their molecular weight and the mass of the formed fractional ions was determined. In this case, the peak of the ion separated from 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.

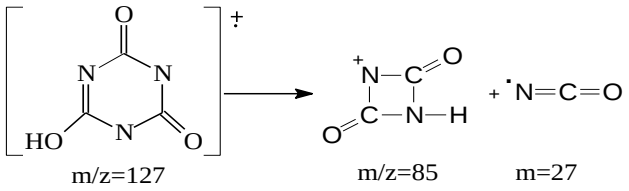
After 2-hydroxy-4,6-bitz (vinyloxy) -1,3,5-triazine was introduced into the gas chromatography-mass spectrometer, under the selected conditions in 0.712 minutes by separation of the vinyl radical, the 2-hydroxy-4 , 6-bits (vinyloxy) - 1,3,5-triazine with m\z 154.



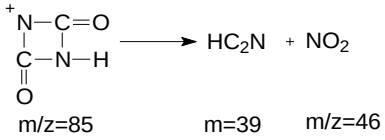
In turn, a vinyl radical is separated in one direction from 2-hydroxy-4,6-bits (vinyloxy) -1,3,5-triazine in 0.175 minutes and the 6-hydroxy-1,3,5-triazine-2 ion is formed , 4-diol with m\z 127.



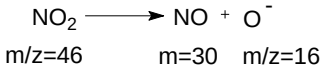
In a chromatography-mass spectrum, fractional ions formed from a molecular ion also form small ionic fragments. As a result of the separation of the N = C = O radical from the 6-hydroxy-1,3,5-triazine-2,4-diol ion, an ion with m\z 85 is formed.



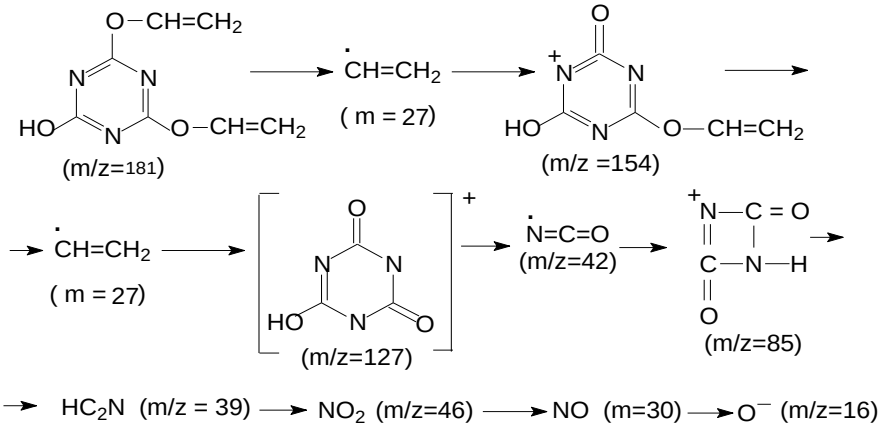
Likewise, nitric oxide (IV) is formed by the separation of the HC_2N molecular ion from 1,3-diazetidine-2,4-diol.



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

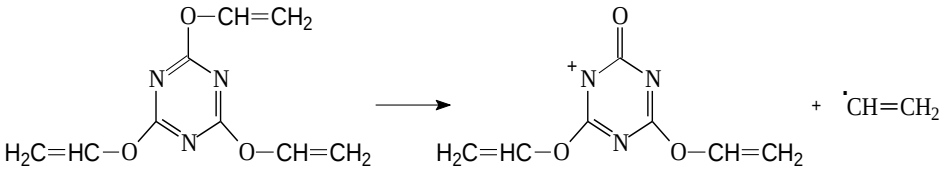


The decomposition into fractional ions of 2,4-hydroxy-6- (vinyloxy) -1,3,5-triazine in the chromatography-mass spectrum can be depicted as follows:

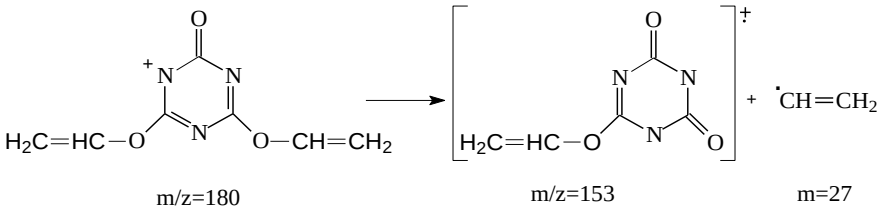


In the chromatography-mass spectrum of cyanuric acid trivinyl ester (2,4,6-tris- (vinyloxy) -1,3,5-triazine), the formation of ions corresponding to their molecular mass and the mass of fractional ions formed during their decomposition was determined. In this case, the peak of the ion separated from 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

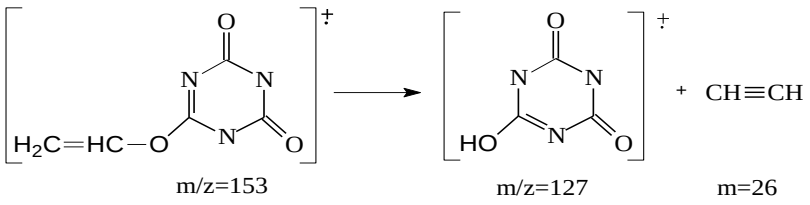
m\z 153 are formed in the spectrum; m\z 127.1; m\z 85.1; m\z 46 and m\z 16. After the introduction of 2,4,6-tric- (vinyloxy) -1,3,5-triazine into the chromatography-mass spectrum, under the selected conditions in 0.712 minutes the vinyl radical is separated and an ion is formed 2-hydroxy-4,6-bit- (vinyloxy) -1,3,5-triazine with m\z 180.



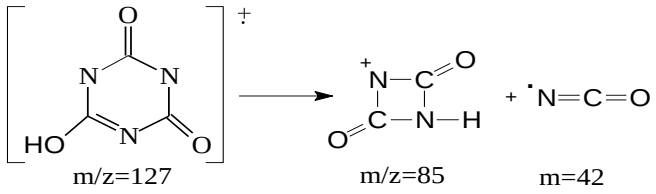
In turn, from the ion of 2-hydroxy-4,6-bit- (vinyloxy) -1,3,5-triazine in 0.175 minutes, from the decomposition of the radical vinyl fraction in one direction, an ion of 2,4-hydroxy-6- (vinyloxy) -1,3,5-triazine with m\z 153.



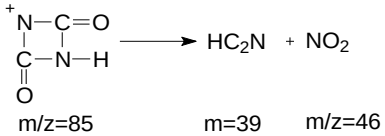
As a result of the separation of the molecular ion of acetylene from 2,4-hydroxy-6- (methylvinyl) -1,3,5-triazine, the formation of an ion with m\z 127 was observed.



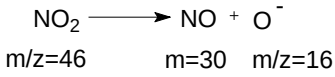
As a result of the separation of the .N = C = O radical from 2,4-hydroxy-6- (vinyloxy) -1,3,5-triazine, 1,3-diazetidine-2,4-dione is formed.



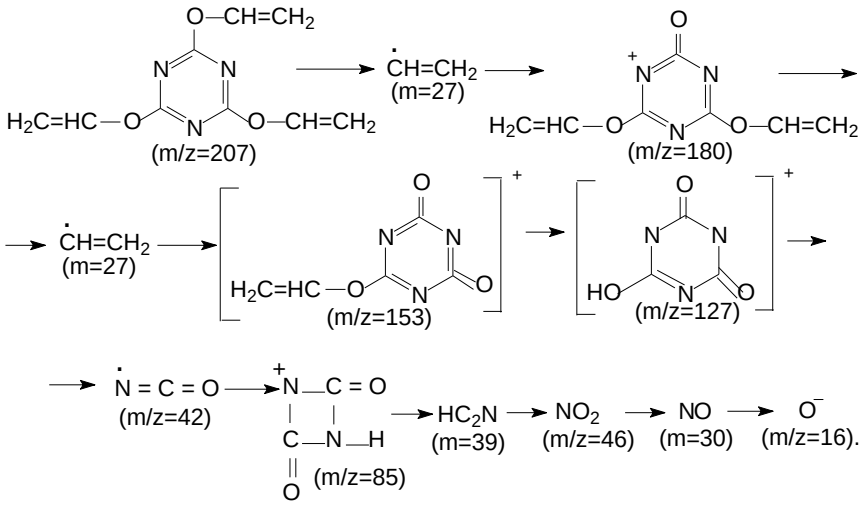
In turn, 1,3-diazetidine-2,4-diol decomposes with the release of the molecular ion HC_2N and nitric oxide (IV) with m/z 46 is formed.



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:



4. 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. It is known that cyanuric acid and its halogenated derivatives are used as biologically active substances. As a result of the introduction of a vinyl group into its molecule, its biological activity is further enhanced. For this reason, the biological activity of vinyl esters of synthesized cyanuric acid was studied. To determine the biological activity of the synthesized compounds, their effect on microorganisms isolated from scrapings from metal structures used in the oil and gas industry was studied. Analysis of the results shows that cyanuric acid can kill 72% of the studied microorganisms. Replacing the hydroxyl group in the cyanuric acid molecule with a vinyl group increases the biological activity of the compound, as well as its resistance to microorganisms. Along with mono-, di- and trivinyl esters of cyanuric acid, the rate of their destruction by microorganisms causing biocorrosion increases and amounts to 76, 77 and 84%, respectively. The activity of the synthesized mixture of vinyl esters averages 79%.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Murphy JL, Arrowood MJ, Lu X, Hlavsa MC, Beach MJ, Hill VR. Effect of Cyanuric Acid on the Inactivation of Cryptosporidium parvum under Hyperchlorination Conditions. Environ. Sci. Technol. 2015;49:7348–7355.
2. Guyader L, Grateloup M, Relative I. Weight of Bacteriological Parameters in Swimming Pool Water Treated by Hypochlorite or Chloroisocyanurates. J. Fr. Hydrol. 2019;23-25.
3. Cho S. Cyanuric acid hydrolase from Azorhizobium caulinodans ORS 571. Crystal structure and insights into a new class of Ser-Lys dyad proteins. Plos. One. 2014;9(6);99349.
4. Prabhaharan M, Prabakaran AR, Srinivasan S, Gunasekaran S. Density functional theory studies on molecular

structure, vibrational spectra and electronic properties of cyanuric acid. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015;138:711-722.
5. Martsinovich N, Kantorovich L. Comparative Theoretical Study of O- and S-Containing Hydrogen- Bonded Supramolecular Structures Jour. Phys. Chem. 2008;112.
6. Fruchey I, Shapir N, Sadowsky MJ, Wackett LP. On the origins of cyanuric acid hydrolase: purification, substrates, and prevalence of AtzD from Pseudomonas sp. strain ADP. Appl Environ Microbiol. 2003;69(6):3653–3657.
7. Duen-Ren H. Ch, Sun WS, Sie JY, Jian Y. Hsu. Direct Formulation of Enol Ethers Using Cyanuric Chloride and N, N-Dimethylformamide. Journal of the Chinese Chemical Society. 2004;51:671-674
8. Liliana PM. Armando C, Luis Enrique S, Roberto S. Aromaticity in cyanuric acid. Journal of Molecular Modeling. 2012;17 (6):1311-1315.
9. Murphy JL, Arrowood MJ, Lu X, Hlavsa MC, Beach MJ, Hill VR. Effect of Cyanuric Acid on the Inactivation of Cryptosporidium parvum under Hyperchlorination Conditions. Environ. Sci. Technol. 2015;49:7348-7355.
10. AE Ziyadullaev, Nurmanov SE, D Kh. Mirkhamitova AD. Hamdanov, K. Kh. Ziyadullaeva, The role of highly basic systems in the vinylation of nitrogen-containing heterocyclic compounds, Zh. Chemistry and chemical technology, Toshkent 2018;4:24-28.
11. Ziyadullaev AE, Nurmanov SE, Zhumartova UU, Parmanov AB. Theoretical foundations of the reaction of homogeneous catalytic vinylation of cyanuric acid, Journal of the Eurasian Union of Scientists, Russia No. 2019;9 (66):37-41s.
12. Krylov OV. Heterogeneous catalysis. Moscow. Academ book. 2004;S(679):176-177 b.
13. Shvets VB. Introduction to the chemistry of catalytic reactions. Soros Educational Journal. 1996;C:33-40.
14. Ziyadullaev AE, Nurmonov SE, Parmonov AB. Study of the catalytic reaction of acetylene. Journal of science. Lyon, France. 2020;8:11-15.
15. Ziyadullaev AE. The use of solutions and catalysts in the synthesis of vinyl esters of 2-4-6-hydroxy-1-3-5-triazine. UNIVERSUM: Technical Science Scientific Journal. Moscow. 2020;12(81):36-40.
16. Ziyadullaev A, Nurmonov S, Kalyadin V, Parmonov A, Jumartova U. Homogeneous catalytic vinylation of 2,4,6-trihydroxy-1,3,5-triazine by acetylene at high pressure. The scientific heritage. 2020;44: 11-17.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/80796