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THEORETICAL FOUNDATIONS OF THE HOMOGENEOUS CATALYTIC VINYLATION REACTION OF CYANURIC ACID

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Abstract: *The paper information of the synthesis vinyl ester of cyanuric acid, by catalytic vinylation involving acetylene under the influence of various catalysts at atmospheric pressures, the use of highly basic systems, alternative conditions for the process and reaction mechanisms of formation of vinyl compounds of cyanuric acid is presented.*

Key words: *acetylene, vinylation, esters of cyanuric acid, mono,- di- and three vinyl cyanurates.*

Introduction

At present, vinyl ethers are widely used in various industries, including: as biologically active substances in medicine; as monomers for the production of polymers and plastic materials; as inhibitors in the oil and gas industry; as crosslinking agents in the production of rubber and synthetic rubber; as adhesives in microelectronics; and as various solvents in the textile industry [1,2]. Vinyl compounds of cyanuric acid have been synthesized through catalytic vinylation involving acetylene, utilizing the active hydrogen atoms of cyanuric acid [3,4].

Scientific Novelty.

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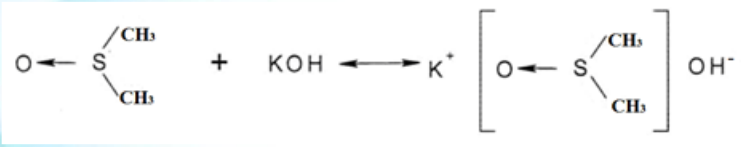
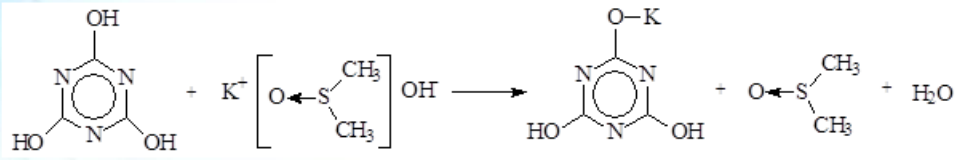
The influence of the nature of the solvent and catalyst, temperature, and the rate of acetylene feed on the formation of vinyl compounds based on cyanuric acid has been studied.

Research Results and Discussion:

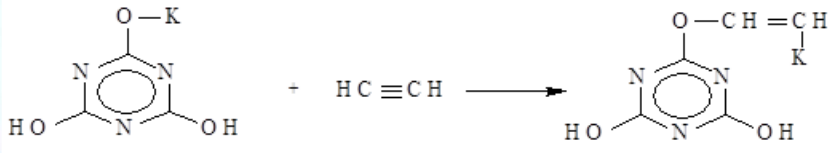
DMSO and DMF were used as solvents, while LiOH, NaOH, and KOH were used as catalysts. As a result, the formation of mono-, di-, and trivinyl ethers of cyanuric acid was established. The formation of vinyl ethers of cyanuric acid is explained as follows: Initially, due to the interaction of KOH with DMSO, a highly basic system is formed:



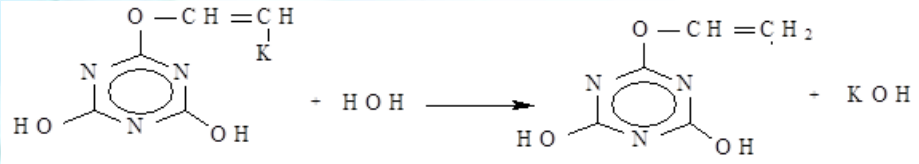
Which, under the influence of a cyanuric acid molecule, forms a potassium compound through the active hydrogen atom of the hydroxyl group:



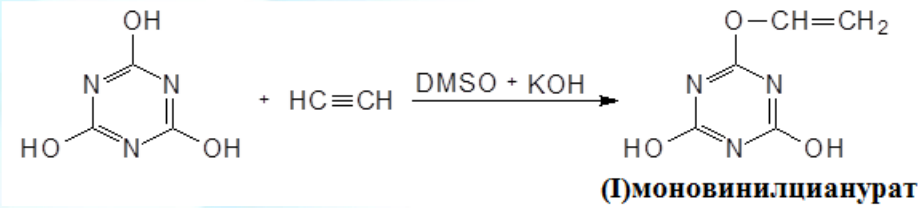
Under the influence of acetylene, the potassium compound of cyanuric acid undergoes nucleophilic addition:



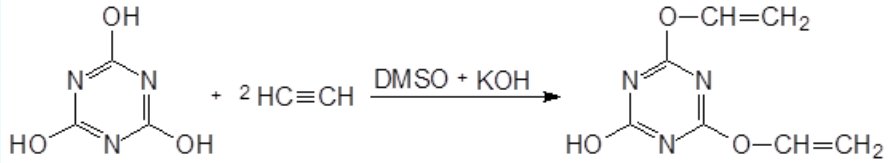
After this, as a result of the hydrolysis of the intermediate compound, a mono-vinyl ether of cyanuric acid is formed:



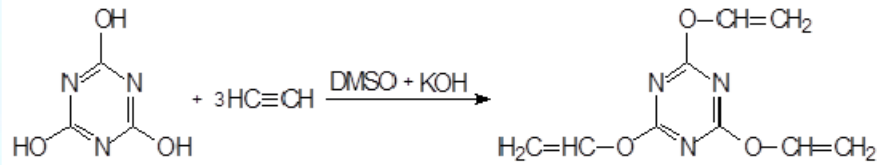
During the process, due to the involvement of the second and third hydroxyl groups, di- and tri-vinyl ethers are formed:



(I)моновинилцианурат



(II) дивинилцианурат



(III) тривинилцианурат

The reactions were carried out at 120 °C in the presence of various solvents (DMSO and DMFA) for a duration of 4–8 hours. The starting compounds were used in equimolar ratios.

As a result, when using DMSO, the product yield was significantly higher than when using DMFA. Additionally, the yield of vinyl ethers increased considerably with an increase in reaction time from 4 to 6 hours; however, a sharp decrease in the formation of vinyl ethers was observed at 8 hours.

Table 1

Effect of Solvent and Reaction Duration on the Yield of Vinyl Ethers of Cyanuric Acid (Temperature 120 °C)

Synthesized Vinyl Ethers	**Product Yield, %**	
	In DMFA	In DMSO
Reaction Time: 4 hours		
I	10.2	16.0
II	11.8	18.0
III	12.2	18.5
Reaction Time: 6 hours		

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Synthesized Vinyl Ethers	Product Yield, %	
I	12.6	18.2
II	14.5	21.8
III	12.6	22.6
Reaction Time: 8 hours		
I	10.6	12.0
II	11.2	12.7
III	13.4	13.2

The influence of temperature, as well as the nature of the solvent and catalyst, on the product yield was studied and analyzed. The results showed that when the reaction was carried out using DMSO for 6 hours, the yield of vinyl ethers reached a maximum: I – 18.2%; II – 21.8%; III – 22.6%.

The reaction of cyanuric acid with acetylene was carried out for 4, 6, and 8 hours at temperatures ranging from 80 to 140 °C. When the reaction was conducted in the presence of KOH in DMFA and DMSO at 80 °C, the yield of vinyl ether was 26.9% and 39.2%, respectively. At 120 °C, the yields increased to 39.7% and 62.6%, respectively.

However, when the temperature was raised to 140 °C, the yield of vinyl ethers sharply decreased due to the partial decomposition of dimethyl sulfoxide.

THE INFLUENCE OF TEMPERATURE, CATALYST TYPE, AND SOLVENT NATURE ON PRODUCT YIELD *(REACTION DURATION: 6 HOURS, CATALYST AMOUNT: 10% OF THE MASS OF CYANURIC ACID)*

Catalyst	**Temperature, °C**	**I**	**II**	**III**	**Total %**
Solvent: DMFA					
KOH	80	6.5	8.4	12.0	26.9
NaOH LiOH	100	8.2	10.2	10.8	29.2
KOH	120	12.6	14.5	12.6	39.7

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Catalyst	Temperature, °C	I	II	III	Total %
NaOH	140	10.4	10.2	6.8	27.4

It should be emphasized that the yields of vinyl ethers of cyanuric acid using KOH as the catalyst and DMSO as the solvent are the highest.

DMFA and DMSO are aprotic solvents with high dielectric permittivity and have a positive effect on the course of nucleophilic reactions. In all cases, when using DMSO, the yields... *(sentence incomplete — please send the next part if you want the rest translated).*

The yield of the products was higher when DMSO was used compared to DMFA. This is due to the fact that DMSO, in combination with the catalyst, forms a highly basic system, which increases the solubility of acetylene [5,6].

The effect of temperature, nature of the catalyst, and solvent on the synthesis of vinyl ethers of cyanuric acid can be explained as follows:

- Potassium hydroxide (KOH) exhibits higher catalytic activity than NaOH and LiOH;
- DMFA, as a solvent, acts as a weak protonic acid and undergoes autoprotolysis due to the positive charge on the nitrogen atom. As a result, it does not form active homogeneous conditions and slows down the rate of vinylation;
- DMSO contains two nucleophilic centers – a hard oxygen atom and a soft sulfur atom. The hydrogen atoms are highly prone to protonation, and in the presence of alkali, catalytic active intermediate complexes are formed, creating favorable conditions for acetylene addition [7].

The obtained results showed that with an increase in the amount of catalyst (5–15%), the product yield increases. At a reaction duration of 6 hours, in the presence of DMSO as solvent and 10% KOH, the monovinyl ether was synthesized with a yield of 18.2%; the divinyl ether – 21.8%; and the trivinyl ether – 22.6%.

Further increase in the reaction time and catalyst amount negatively affects the formation of products.

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The activation energy and reaction rate were calculated in order to determine the kinetic parameters for the synthesis of mono-, di-, and tri-vinyl ethers of cyanuric acid (Tables 4–6).

Table 4

Kinetic Parameters of the Synthesis Process of Monovinyl Ether of Cyanuric Acid (Solvent: DMSO, Catalyst: KOH)

Reaction Duration (h)	Temperature (°C)	Product Yield (%)	Product Yield (mol/L)	Average Reaction Rate (%/h)	Average Reaction Rate (mol/L·h)
4	80	12.6	1.03	4.56	0.23
	100	15.3	1.25	5.53	0.27
	120	16.0	1.30	5.87	0.28
	140	13.6	1.10	4.98	0.23
6	80	12.2	0.99	4.41	0.22
	100	16.7	1.35	6.03	0.30
	120	18.2	1.47	6.57	0.32
	140	16.4	1.32	5.92	0.28
8	80	10.6	0.80	3.81	0.19
	100	11.2	0.85	4.02	0.20
	120	12.0	0.92	4.30	0.21
	140	10.8	0.83	3.89	0.20

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Table 5

Kinetic Parameters of the Synthesis of Divinyl Ether of Cyanuric Acid *(Solvent: DMSO, Catalyst: KOH)*

Reaction Duration (hours)	Temperature (°C)	Product Yield (%)	Product Concentration (mol/L)	Average Reaction Rate (%/h)	Average Reaction Rate (mol/L·h)
4	80	12.6	1.03	4.56	0.23
	100	14.2	1.16	5.14	0.26
	120	18.0	1.48	6.52	0.33
	140	12.2	1.00	4.41	0.22
6	80	14.6	1.19	5.28	0.26
	100	18.6	1.51	6.73	0.34
	120	21.8	1.78	7.89	0.40
	140	16.0	1.30	5.27	0.29
8	80	9.8	0.80	3.54	0.17
	100	10.2	0.83	3.69	0.18
	120	12.7	1.04	4.60	0.23
	140	12.2	0.99	4.41	0.22

Table 6

Kinetic Parameters of the Synthesis of Trivinyl Ether of Cyanuric Acid *(Solvent: DMSO, Catalyst: KOH)*

Reaction Duration (hours)	Temperature (°C)	Product Yield (%)	Concentration (mol/L)	Yield per hour (%/hour)	Reaction Rate (mol/L·hour)
4	80	12.4	1.01	4.48	0.22
	100	14.6	1.19	5.28	0.26
	120	18.5	1.50	6.69	0.32
	140	16.2	1.66	5.85	0.28

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Reaction Duration (hours)	Temperature (°C)	Product Yield (%)	Concentration (mol/L)	Yield per hour (%/hour)	Reaction Rate (mol/L·hour)
6	80	12.4	1.01	4.48	0.22
	100	14.8	1.20	5.33	0.26
	120	22.6	1.86	8.15	0.42
	140	10.8	0.88	3.89	0.20
8	80	10.2	0.83	3.69	0.18
	100	11.8	0.96	4.27	0.21
	120	13.2	1.07	4.77	0.23
	140	12.6	1.03	4.56	0.22

Conclusion:

The kinetic parameters of the synthesis of vinyl esters of cyanuric acid were analyzed. The average reaction rates were determined, and the activation energies were calculated. It was established that at a reaction duration of 6 hours and a temperature of 120 °C, the yields of the vinyl esters reach their maximum values:

1. **mono-vinyl ester** — 18.2%,
2. **di-vinyl ester** — 21.8%,
3. **tri-vinyl ester** — 22.6%

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