SOLVENT EFFECTS ON HIGH-PRESSURE CATALYTIC VINYLATION OF CYANURIC ACID

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Abstract. Background of the Problem.

Cyanuric acid and its derivatives are widely used in various industrial sectors. They serve as monomers in polymer synthesis, agents for microbiological treatment of natural water bodies and industrial wastewater, and chlorine stabilizers. Additionally, they are used in the production of industrial dyes, surfactants, pesticides, and herbicides for agricultural applications.

Objective:

To synthesize vinyl derivatives of cyanuric acid under homogeneous catalytic conditions through its reaction with acetylene at high pressures and to determine the optimal reaction parameters.

Methodology:

Vinyl esters of cyanuric acid were synthesized via a homogeneous catalytic method under high-pressure conditions. The structure of the synthesized compounds was confirmed using infrared (IR) spectroscopy.

Scientific Novelty:

Mono-, di-, and trivinyl esters of cyanuric acid were synthesized for the first time via catalytic vinylation of acetylene in the presence of solvents.

Results:

The synthesis of mono-, di-, and trivinyl esters of cyanuric acid under high-pressure conditions was investigated. The influence of catalyst concentration, solvent nature, reaction temperature, and duration on product yield was studied.

Keywords:

Cyanuric acid and its vinyl esters; vinylation; acetylene; high pressure; catalytic reactions.

Highlights:

- *Mono-, di-, and trivinyl esters of cyanuric acid were synthesized.*
- *The mechanism of cyanuric acid vinylation was discussed.*
- *Factors affecting the yield of vinyl esters of cyanuric acid were evaluated.*

Introduction:

The properties of cyanuric acid and its derivatives have been extensively studied by prominent scientists such as J. Liebig, F. Wöhler, A. W. Hofmann, I. V. Gauthier, O. Laurent, C. F. Gerhardt, C. A. Wurtz, and F. F. Beilstein. Nevertheless, the vinylation, isomerism, and other chemical characteristics of cyanuric acid and its derivatives require further in-depth investigation [1–4].

Cyanuric acid is widely used as a key reagent in the thermal processing of polymers such as polyphenylacetylene, microcrystalline cellulose, polyvinyl alcohol, polysulfone, polycarbonate, and polyvinyl chloride. Its presence in many technological processes not only accelerates chemical reactions under high-pressure conditions but also enhances the reactivity of chemical systems. For this reason, the chemical activity of cyanuric acid under elevated pressures has been a subject of particular interest in various studies [5–6].

Materials and Methods

The vinylation reaction of cyanuric acid was carried out under homogeneous catalytic conditions in an RCG 1.6-100/6 K1-type reactor at a pressure of 10 atm. The process was conducted with acetylene gas at varying temperatures and reaction times. Acetylene (supplied from a cylinder) was used as the vinylating agent, while zinc oxide (ZnO) served as the catalyst. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used as solvents.

The resulting reaction mixture was extracted with diethyl ether. The organic phase was separated, and the solvent was removed. The residue was then subjected to vacuum fractional distillation for further purification.

Infrared (IR) spectra of the synthesized compounds were recorded using “Specord-75”, “Shimadzu”, or “UR-70” spectrophotometers in the range of 400–4000 cm^{-1}. The samples were analyzed either in solution or as neat films.

IR Spectroscopic Characterization

Monovinyl ester of cyanuric acid:

Characteristic IR absorption bands (cm^{-1}):

3512 (–OH), 1765 (C=O), 1384 (C=N), 1093 (C–OH), 1253 (C–O–C), 864 (=CH$_2$), 1471 (=CH), 1660 (–CH=CH$_2$).

Divinyl ester of cyanuric acid:

Characteristic IR absorption bands (cm^{-1}):

3493 (–OH), 1759 (C=O), 1386 (C=N), 1091 (C–OH), 1253 (C–O–C), 864 (=CH$_2$), 2929 and 1438 (=CH), 1654 (–CH=CH$_2$).

Trivinyl ester of cyanuric acid:

Characteristic IR absorption bands (cm^{-1}):

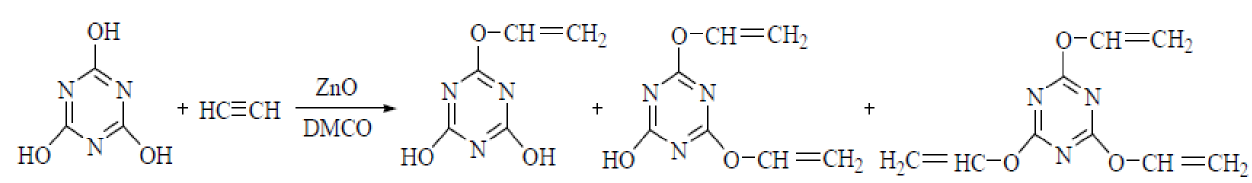
1791 (C=O), 1400 (C=N), 1056 (C–O–C), 761 (=CH$_2$), 3053 and 1463 (=CH), 1693 (–CH=CH$_2$).

Results and Discussion

The synthesis of vinyl derivatives of cyanuric acid was initially performed under atmospheric pressure conditions, as previously reported [7–9]. Further reactions were carried out at pressures ranging from 1 to 20 atm in the presence of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as solvents, with zinc oxide (ZnO) as a catalyst.

As a result of these experiments, mono-, di-, and trivinyl esters of cyanuric acid were successfully obtained. The vinylation reaction proceeds via a nucleophilic substitution mechanism.

The proposed reaction scheme and the possible mechanistic pathway are illustrated below:

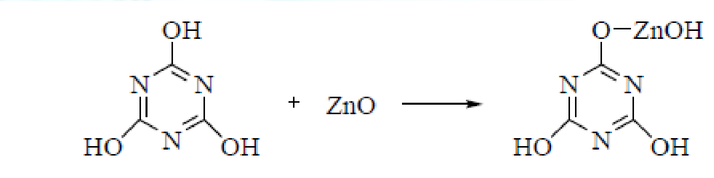


The influence of pressure, temperature, and solvent type on the product yield was systematically studied. It was found that increased pressure and the use of polar aprotic solvents significantly improved the yield and selectivity of vinylated products.

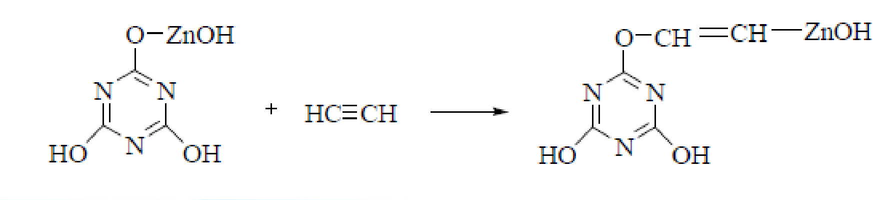
The nucleophilic substitution mechanism is favored due to the electron-deficient triazine ring of cyanuric acid, which facilitates attack by the vinylating agent (acetylene) at the hydroxyl functional groups. The formation of mono-, di-, and trivinyl esters is largely dependent on the molar ratio of acetylene to cyanuric acid and the duration of the reaction.

These findings demonstrate the effectiveness of ZnO as a catalyst under relatively mild conditions and highlight the importance of optimizing reaction parameters for selective synthesis of cyanuric acid vinyl esters.

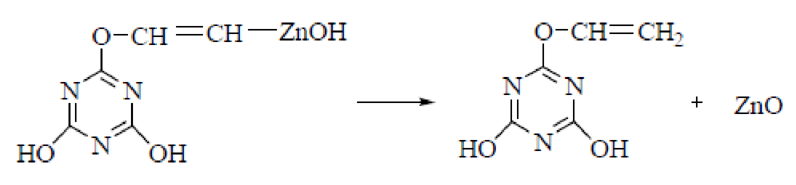
The vinylation reaction likely proceeds through the initial coordination of cyanuric acid with ZnO, forming a reactive intermediate. This coordination activates the hydroxyl groups on the triazine ring, making them more susceptible to nucleophilic attack by acetylene. The sequential substitution results in the formation of mono-, di-, and trivinyl esters, depending on the stoichiometry and reaction conditions.



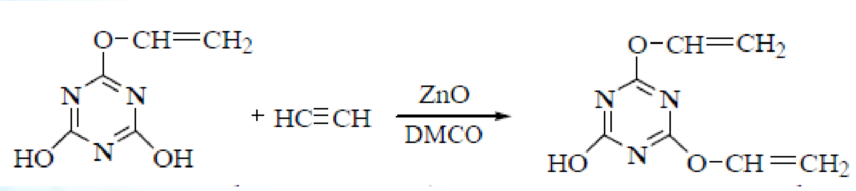
The resulting zinc hydroxide compound reacts with acetylene to form an intermediate product, namely a vinyl-substituted zinc hydroxide derivative.



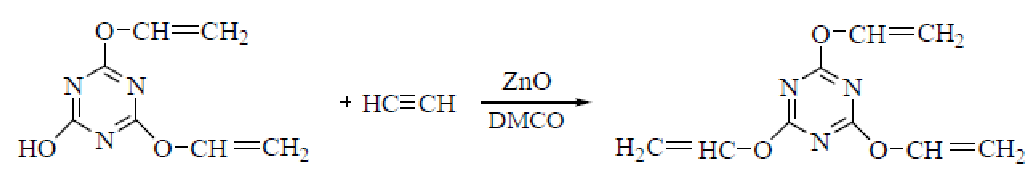
Under elevated temperature and high pressure, the vinylated zinc hydroxide complex transforms into the monovinyl ester of cyanuric acid, with the concurrent release of zinc oxide.



The reaction of the monovinyl ester with acetylene leads to the formation of the divinyl ester of cyanuric acid.



According to this mechanism, the divinyl ester can further react to form the trivinyl ester of cyanuric acid.



The vinylation reaction of cyanuric acid was carried out at a pressure of 1–20 atm for 2–6 hours at a temperature range of 100–160°C. To accelerate the reaction, increase the efficiency of the process, and minimize the risk of acetylene decomposition, the reaction mixture was diluted with an inert gas—nitrogen.

The effects of reaction time, temperature, and pressure on the synthesis of vinyl esters during the vinylation of cyanuric acid in the presence of DMSO + ZnO and DMF + ZnO were investigated.

When the reaction was conducted for 2 hours in the presence of DMSO and ZnO at a pressure of 10 atm, the yield of the monovinyl ester was higher than that of the di- and trivinyl esters (see Fig. 1).

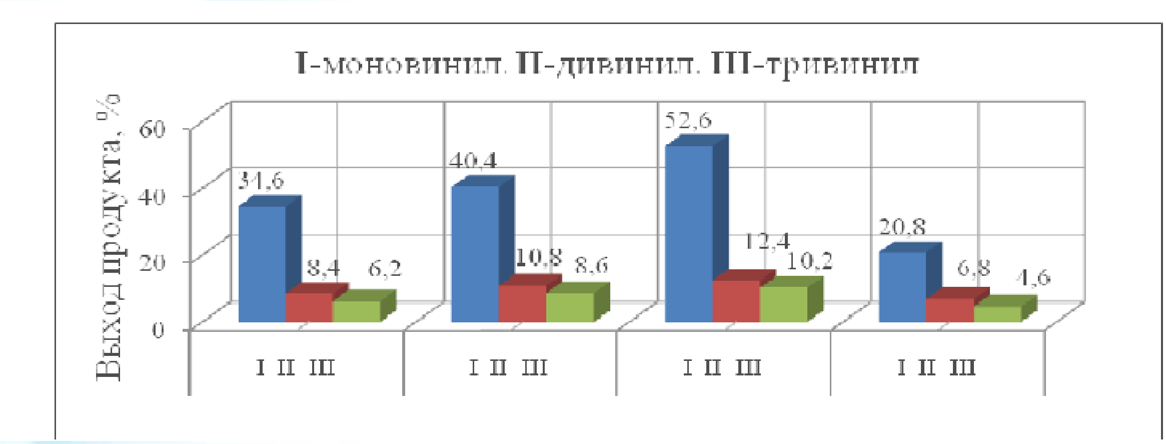


Figure 1. *Effect of DMSO + ZnO on the yield of vinyl esters of cyanuric acid*

Analysis of the results shows that the introduction of acetylene in the presence of the DMSO + ZnO system for 2 hours at temperatures of 100, 120, and 140°C and a pressure of 10 atm leads to the synthesis of monovinyl ester with yields of 34.6%, 40.4%, and 52.6%, respectively; divinyl ester – 8.4%, 10.8%, and 12.4%; and trivinyl ester – 6.2%, 8.6%, and 10.2%. When the reaction was carried out at 160°C, the yields of the vinyl esters decreased to 20.8%, 6.8%, and 4.6%, respectively.

Vinylation of cyanuric acid was also performed with a reaction time of 4 hours in a DMSO solution in the presence of ZnO at temperatures ranging from 100 to 160°C (Table 1).

Table 1. Effect of temperature on the yield of vinyl esters of cyanuric acid in the DMSO + ZnO system (reaction duration 4 hours)

Temperature (°C)	**Monovinyl ester (%)**	**Divinyl ester (%)**	**Trivinyl ester (%)**
100	61.5	13.6	10.4
120	64.7	15.9	12.6
140	68.4	18.4	13.3
160	44.5	11.2	7.8

Results and Discussion

The results showed that as the temperature increased in the range of 100–160 °C over a reaction duration of 4 hours, the yield of vinyl esters of cyanuric acid passed through a maximum. At 140 °C, the yields of mono-, di-, and trivinyl esters were 16.4%, 46.8%, and 18.0%, respectively. A further increase in temperature led to a decrease in the yields. For example, at 160 °C, the yields of mono-, di-, and trivinyl esters decreased to 6.6%, 20.8%, and 8.6%, respectively.

It is noteworthy that in all cases, the yield of the divinyl ester was higher than that of the mono- and trivinyl esters.

Additionally, the synthesis of vinyl esters of cyanuric acid was studied in the presence of the DMF–ZnO system (Fig. 2).

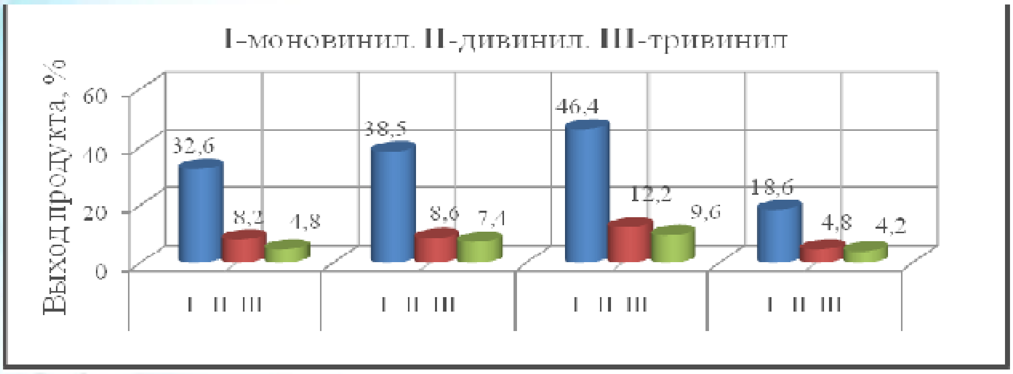


Fig. 2. Effect of DMF + ZnO on the yield of vinyl esters of cyanuric acid (reaction duration: 2 hours)

Analysis of the results showed that at 100 and 140°C, the yields were as follows: (I) monovinyl ester – 32.6% and 46.5%; (II) divinyl ester – 8.2% and 12.2%; (III) trivinyl ester – 4.8% and 4.2%, respectively. The effect of temperature on the reaction of cyanuric acid with acetylene under high pressure for 4 hours in the DMF + ZnO system was also studied (Table 2).

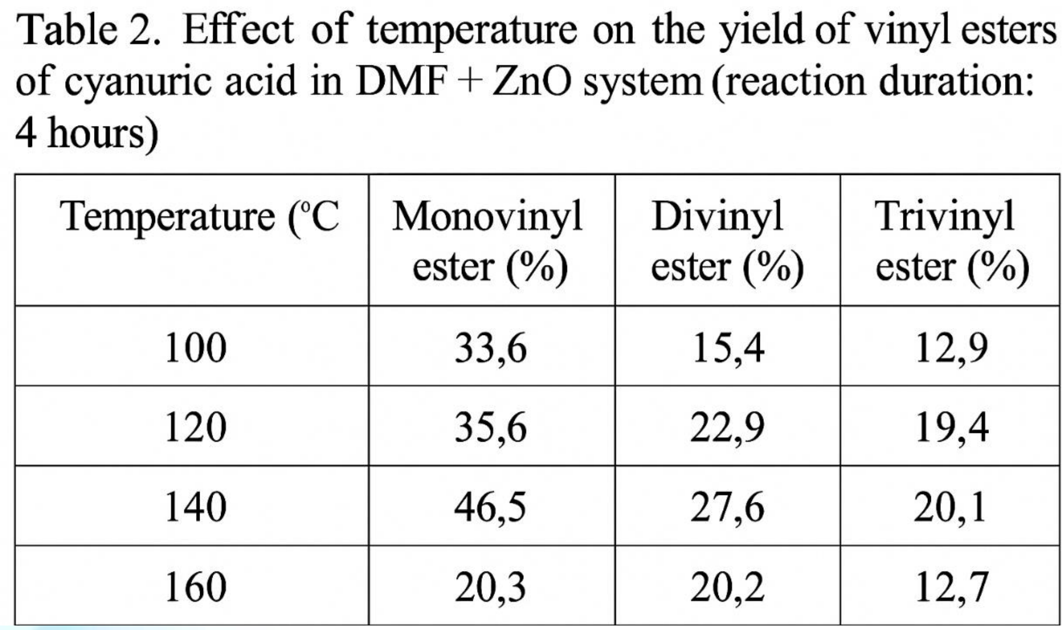


Table 2. Effect of temperature on the yield of vinyl esters of cyanuric acid in DMF + ZnO system (reaction duration: 4 hours)

Temperature (°C	Monovinyl ester (%)	Divinyl ester (%)	Trivinyl ester (%)
100	33,6	15,4	12,9
120	35,6	22,9	19,4
140	46,5	27,6	20,1
160	20,3	20,2	12,7

Results showed that when using DMF as a solvent, the process productivity was significantly lower compared to DMSO. The catalytic effect of DMSO is explained by the fact that during the vinylation of cyanuric acid, acetylene is activated more effectively in the DMSO+ZnO system than in the DMF+ZnO system. The influence of temperature (100–160°C) on the yield of vinyl ethers was also investigated for a reaction duration of 6 hours in both DMF+ZnO and DMSO+ZnO systems (see Fig. 3).

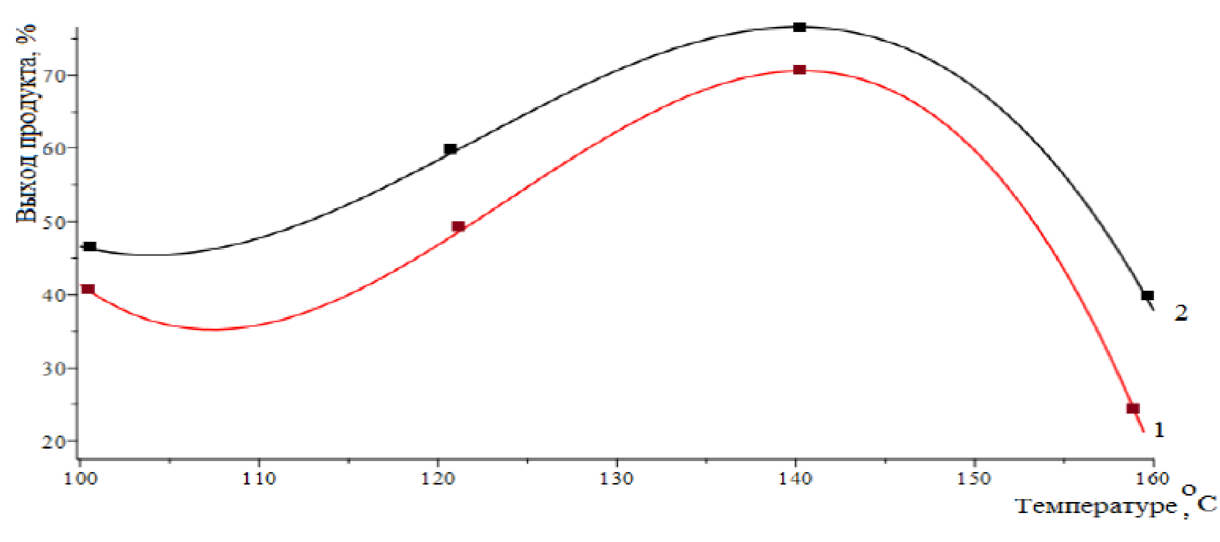


Figure 3. Effect of temperature on the yield of divinyl ether of cyanuric acid with a reaction duration of 6 hours in the systems DMFA + ZnO (1) and DMSO + ZnO (2).

The comparative analysis of experimental results showed that, with a reaction duration of 6 hours, the yield of the product in both systems increased with temperature and reached a maximum at 140 °C — 70.6% in the DMF system and 76.5% in the DMSO system.

It should be noted that when the reaction time was extended to 6 hours and the temperature was raised from 100 to 160 °C, the yield of the trivinyl ether in DMSO was higher than that of the mono- and divinyl ethers. In particular, at 100, 120, and 140 °C, the trivinyl ether yield was 46.6%, 58.4%, and 76.5%, respectively. However, further temperature increases beyond 160 °C led to a sharp decrease in the yield of the products.

Conclusion. In the vinylation of cyanuric acid, the DMSO + ZnO system was found to be significantly more efficient than the DMF + ZnO system. Under a pressure of 10 atm and a temperature of 140 °C, the optimal reaction durations for synthesizing the mono-, di-, and trivinyl ethers were determined to be 2 hours (52.6%), 4 hours (46.8%), and 6 hours (76.5%), respectively.

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