INTERNATIONAL MULTIDISCIPLINARY JOURNAL FOR RESEARCH & DEVELOPMENT
SJIF 2019: 5.222 2020: 5.552 2021: 5.637 2022:5.479 2023:6.563
eISSN 2394-6334 https://www.ijmrd.in/index.php/imjrd Volume 10, issue 09 (2023)

KINETICS OF MORPHOLINE VINYLATION PROCESS

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Abstract: Morpholine at work vinylation reaction with acetylene at atmospheric pressure in a homogeneous-catalytic method was systematically studied. The effect of key factors on N-vinylmorpholine yield was identified and optimized. The kinetics of the vinylation process were studied.

Key words: N-vinylamines, nitrogen-containing compounds, chemistry, heterogeneous method.

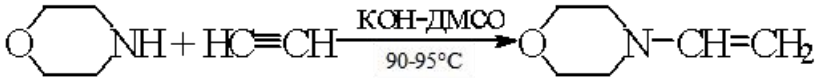
Introduction. It is known in the literature that the synthesis of vinyl compounds of nitrogen-containing organic substances was carried out under high pressure and the corresponding N-vinylamines were obtained with high yield [1,2]. It should be noted that rare and expensive equipment and devices are needed to carry out such processes. Due to the fact that acetylene and its derivatives have explosive and flammable properties at high pressure, technical safety must be strictly observed [3].

In the last 20 years, the use of alkali-aprotic dipolar solvent, highly basic systems in acetylene chemistry has made it possible to synthesize hard-to-obtain vinyl compounds, as well as nitrogen-containing heterocyclic compounds and their N-vinyl derivatives . However, relatively little study of the alkali-DMSO system cannot fully explain some of the laws of vinylation reactions.

Literature sources do not provide information on methods of vinylation reactions of nitrogen-containing compounds, including morpholine, in homogeneous and heterogeneous systems in highly basic systems. In particular, there is no information on the conditions of carrying out the process in the heterogeneous method, the nature of the used catalysts, the explanation of the laws of the reaction, the kinetics of the vinylation process, and the methods of finding the activation energy. Based on these, the catalytic reaction of morpholine with acetylene in the presence of alkaline catalysts and the kinetics of the process were studied.

Materials and methods. It is known that substances containing an active hydrogen atom are used for the synthesis of vinyl compounds. The substance used in the study, morpholine, is an example of compounds in this category. The morpholine molecule has a center occupied by one active hydrogen atom. Based on these, in order to compare the results of morpholine obtained by

homogeneous method, catalytic vinylation reactions in heterogeneous method were systematically studied. It was proved that the main part of the resulting product is a vinyl derivative of morpholine [4]. The process of morpholine vinylization can be schematically presented as follows:



The reaction was carried out in the presence of heterogeneous catalysts in a vertically placed reactor operating in flow. Alkalis soaked in granular activated carbon were used as contacts. One of the main factors is the influence of the nature of the catalysts on the process in the heterogeneous method. In this process, the effect of the nature and amount of catalysts was first studied. Alkaline metal hydroxides (LiOH, NaOH, KOH) were used as catalysts. The results of the study of the influence of the nature of the catalysts used in the process are shown in the following table 1.

Table 1

The influence of the nature of catalysts on the yield of N-vinylmorpholine (catalyst amount - 15% relative to the mass of morpholine,

time duration - 3 hours, temperature 90 ° C)

No	Used catalysts	N-vinylmorpholine yield , %
1.	LiOH	16.6
2.	NaOH	19.4
3.	KO H	23.0

According to the obtained results, KON was relatively active among the used catalysts, with the maximum product yield of 23.0%, as well as 16.6 and 19.4% for LiOH and NaOH catalysts, respectively.

Among the methods of preparation of heterogeneous catalysts, catalysts were prepared by soaking method, which is more effective in laboratory conditions. Activated carbon (AU-L, AU

brand), which is widely used in industry, was used as an adsorbent. The prepared catalysts were applied to the process of vinylation of morpholine.

The processes of vinylation of heterocyclic amines are carried out at much higher temperatures. Therefore, it is important to study the effect of temperature on such processes. The process of vinylation of morpholine was studied in highly basic systems (KON-DMSO and KON-DMFA) under homogeneous conditions at atmospheric pressure.

The influence of the nature of the solvent on the vinylation of morpholine was studied. Dimethylformamide (DMFA) and dimethylsulfoxide (DMSO) were used as solvents. DMSO solvent was found to be relatively more active, product yield was 22.8%. It was carried out at different time durations (2, 4, 6, 8 hours) and temperatures (60 ° C, 70 ° C, 80 ° C, 90 ° C). Alternative conditions for the homogenous vinylation reaction of morpholine: temperature - 90 ° C, time duration - 4 hours, catalyst content (KON) - 15%, in which the maximum yield of the product was 31.7%. The effect of temperature on the process of heterogeneous-catalytic vinylation of morpholine was investigated. The reaction was carried out in the presence of a flow reactor and heterogeneous catalysts. In this case, KON (30% by mass) soaked in granular activated carbon was used as a contact, and it was found that N-vinylmorpholine was also formed in this process. The obtained results are presented in Table 2.

Table 2

Temperature dependence of the yield of N-vinylmorpholine

No t/r	Temperature , ° S	Yield of N- vinylmorpholine , %
1	65-70	-
2	100-105	10.6
3	120-125	18.4
4	140-160	19.8
5	180-190	21.5
6	210-215	23.2
7	225-230	25.0
8	250-255	45.7
9	280-285	19.0
10	290-300	12.0

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Experiments show that with increasing temperature, that is, at 100-250 ° C, the yield of N-vinylmorpholine is 10-45.7%, when it rises to 280-285 ° C, it is 19%, and at 290-300 ° C, it is 12%. did, and the further increase in temperature led to a decrease in product yield. The alternative temperature in the gas phase was 250-255 ⁰ C, and the product yield was 45.7%.

The kinetics of the reaction of morpholine with acetylene was studied. The vinylization process was carried out at different time durations (2, 4, 6, 8 hours) and temperatures (60 ° C, 70 ° C, 80 ° C, 90 ° C). The average rate of the reaction was found (%/h, in units of mol/l·h). The obtained results are presented in the following table (Table 3.

Table 3

Morpholine VinylLash Heating Kinetic Results

Duration of time,	N is a product of vinyl morpholine		The average speed of the reaction (W)	
So a t	%	mol / l	% / hour	mol/l· hour
		Temperature - 60 ° S		
2	2.0	0.2	1.0	0.1 1
4	8.0	0.8	2.0	0.2 2
6	10.2	1.0	1.7	0.19
8	14,1	1.4	1.75	0, 20
		Temperature - 70 ⁰ C		
2	5.0	0.5	2.5	0.2 8
4	12.8	1.3	3.2	0.3 6
6	15.0	1.5	2.5	0, 18
8	16,1	1.6	2.0	0.2 2
		Temperature - 80 ⁰ C		
2	10.0	1.0	5.0	0.5 6
4	22,1	2.2	5.5	0, 62
6	25.2	2.5	4.2	0.4 8

8	24.8	2.5	3.1	0.3 5
		Temperature - 90 ^{0} C		
2	12.0	1.2	6.0	0.6 8
4	31 , 7	2.5	7 , 9	0, 71
6	25.8	2.6	4.3	0.4 9
8	24,1	2.4	3.0	0.3 4

To calculate the activation energy of the process, the value of the decimal logarithm of the average rate of the reaction was obtained. As an example, the calculation of the results of the experiment conducted at a temperature of - 90 ° C was given.

8.68 - 1.04

1000 ml – x $_1$ =119.81 87 2 =0.68·10 $^{-4}$ *(for the 2nd hour)*

8.68 - 2.17

1000 ml – x $_2$ =250 874 =0.71·10 $^{-4}$ *(for the 4th hour)*

8.68 – 2.23

1000 ml –x $_3$ =239.63 876 =0.49·10 $^{-4}$ *(for the 6th hour)*

8.68 - 2.08

1000 ml-x $_4$ =256.91 87 8=0.34·10 $^{-4}$ *(for the 8th hour)*

For the rest of the processes (temperature – 60 ° C, 70 ° C, 80 ° C) the average speed values were calculated in the same way and logarithmized (transformed from lgW to 5+lgW).

$$lgW_1 = \frac{60^0C-4soat}{lg0{,}22\cdot10^{-4}} = -4.65/0.34 \qquad lgW_2 = \frac{70^0C-4soat}{lg\,0{,}36\cdot10^{-4}} = -4.44/0.55$$

$$lgW_3 = \frac{80^0C-4soat}{lg0{,}62\cdot10^{-4}} = -4.20/0.79 \qquad lgW_4 = \frac{90^0C-4soat}{lg0{,}34\cdot10^{-4}} = -4.15/0.85$$

The vinylization process was carried out at different temperatures. Inverse temperature (1/T) values were calculated as follows.

$$1/T = \frac{1}{273+60^0S} = 3.00\cdot10^{-3} \qquad 1/T = \frac{1}{273+70^0C} = 2.91\cdot10^{-3}$$

$$1/T = \frac{1}{273+80^0C} = 2.83\cdot10^{-3} \qquad 1/T = \frac{1}{273+90^0C} = 2.75\cdot10^{-3}$$

The average rate and reverse temperature values for vinylation of morpholine are given in Table 4 below.

Table 4

Average reaction rate and reverse temperature values

Reaction temperature, ° S	W ,mol / l · hour · 10 $^{-4}$	lgW	5+lgW	1/T·10 $^{-3}$
Duration of time - 2 hours				
60	0.11	- 4.96	0.04	3.00
70	0.28	- 4.55	0.44	2.91
80	0.56	-4.25	0.74	2.83
90	0.68	-4.16	0.83	2.73
Duration of time - 4 hours				
60	0.22	-4.65	0.34	3.00
70	0.36	- 4.44	0.55 0.74	2.91
80	0.62	-4.20	0.85	2.83
90	0.71	-4.15		2.73
Duration of time - 6 hours				
60	0.19	-4.72	0.27	3.00
70	0.28	-4.55	0.44	2.91
80	0.48	- 4.31	0.68	2.83
90	0.49	-4.30	0.69	2.73
Duration of time - 8 hours				
60	0.20	-4.70	0.30	3.00
70	0.22	-4.65	0.34	2.91
80	0.35	-4.45	0.54	2.83
90	0.34	-5.47	0.46	2.73

When the results in the table are graphically depicted, it is clear from Figure 3 that the product yield passes through the maximum when the temperature is 90 o C and the time duration is 4 hours, and the average rate of the reaction (W) is 0.62 mol / l·h will be equal.

Based on the obtained kinetic results, the logarithm of the velocity (lgW) was plotted as a function of the inverse temperature (1/T) (Fig. 1)

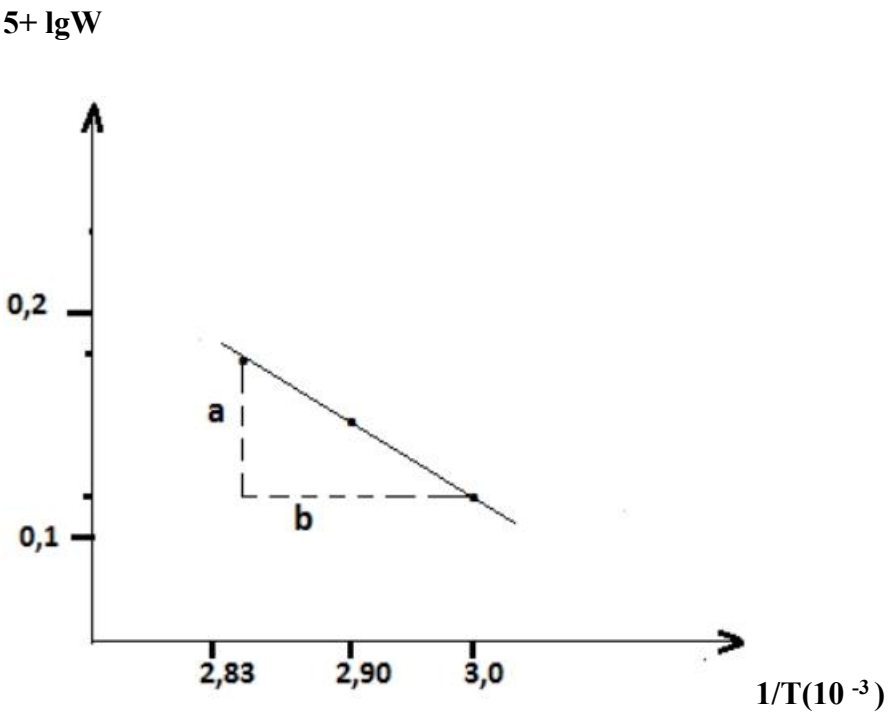

Figure 1 . In the vinylation of morpholine lgW dependence of 1 /T

To calculate the activation energy of vinylation process of morpholine, the time duration - 4 hours, and the temperature - 70 ° C results were used. Based on the calculated kinetic results, a graph was drawn and the angle tangent value was found as follows:

to t $\frac{a}{h} = \frac{0,44-0,34}{(3,0-2,83).10-3} = \frac{0,1}{0,00017} = 588.23$

The reaction activation energy (E) was calculated according to the Arrhenius equation, and its value was found to be 47.1 kJ/mol.

E=2.3t·R=2.3·588.23·8.31=11242.84·4.19=47.1 kJ/mol

where: R=·8.31 J/K·mol

Therefore, the obtained results show that the process of vinylation of morpholine with acetylene in a homogeneous way belongs to the series of processes that proceed in one step, and the activation energy value is not very large.

The structure of N- vinylmorpholine was proved by I Q -spectroscopic method , and its purity was proved by thin layer chromatography . Absorption lines in IR-spectroscopy of N-vinylmorpholine are as follows: valence vibrations of the S=S vinyl group in the 1520-1610 cm $^{-1}$ region, 1050-1250 cm $^{-1}$ region belonging to the S-O-S fragment morpholine molecule, 2950-2960 cm $^{-1}$ – methylene symmetric and asymmetric fluctuations of the group were observed.

The synthesized morpholine vinyl derivative was determined for its biological activity and toxicity and recommended for large-scale study. The method of homogeneous-catalytic vinylation of morpholine was applied to the educational process.

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