GLOBAL RESEARCH NETWORK
ONLINE RESEARCH HUB

AMERICAN JOURNAL OF ECONOMICS AND BUSINESS MANAGEMENT

ISSN: 2576-5973
Vol. 6, No. 10, 2023

The Role of High Base Systems un Vinylation Reactions

D. Kh. Mirkhamitova, D. A. Jadilova, V. N. Juraev
Tashkent State Technical University Almalyk branch

Abstract: The vinylation reaction of piperidine, pyridine and morpholines from nitrogen-containing compounds in highly basic systems has been investigated. The influence of various factors on the course of the process was studied and alternative conditions were found.

Keywords: piperidine, pyridine, morpholine, acetylene, vinylation, homogeneous system, temperature catalyst, solvents, highly basic system, influence of various factors on process progress, alternative conditions.

Known organic compounds, including vinyl derivatives of amines, are widely used in the economy, chemical industry, as valuable monomers. In addition, such substances are used to obtain special polymers, sorbents, dyes, pigments, medicinal preparations, photosensitive materials, biologically active substances and thermostabilizing fibers [1].

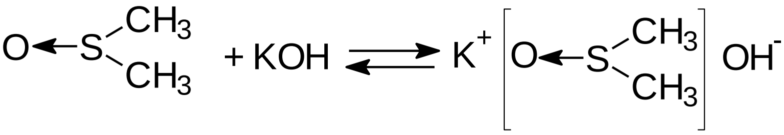
Corresponding N-vinylamines are obtained with sufficiently high yields as a result of vinylation reactions of nitrogen-containing organic substances with acetylene compounds at high pressure. It should be noted that rare and expensive equipment is required to carry out such processes. Due to the fact that acetylene and its derivatives have explosive and flammable properties at high pressure, it is necessary to strictly observe the safety of equipment.

In recent years, there has been increasing interest in the use of highly basic systems in the methods of organic synthesis, in the vinylation of substances containing active hydrogen atoms with the participation of acetylene compounds.

Due to the low reactivity of the hydrogen atom in nitrogen, the vinylization reactions of some nitrogen atom-containing compounds: piperidine, pyridine, morpholines have been little studied. Therefore, the study of their vinylization reactions in the presence of catalysts of different nature, organic solvents, their mixtures, and highly basic environments is one of the important and urgent tasks of modern organic chemistry.

In the last 20 years, the use of alkali-aproton dipolar solvent highly basic systems in acetylene chemistry made it possible to synthesize hard-to-obtain vinyl compounds, as well as nitrogen-containing heterocyclic compounds and their N-vinyl derivatives . However, the relatively little study of the alkali-DMSO system cannot explain some of the laws of vinylation reactions. Based on this, vinylation reactions of some easily available cyclic amines were studied in KON catalyst and KON-DMSO, KON-DMFA highly basic systems [2].

The importance of DMSO in the vinylation process is that in the KON-DMSO system, the base initially dissociates into ions, forming a highly basic, poorly solvated dimacyl-anion:



In general, in such cases, it is necessary to take into account the change of the electrical conductivity of the environment, hydrogen bonding and other factors.

It is known that substances containing an active hydrogen atom, including primary and secondary amino compounds, are used for the synthesis of N - vinyl compounds. Based on these, catalytic vinylation reactions of piperidine, pyridine, morpholines in the presence of acetylene at atmospheric pressure were systematically studied. Below are the results of the piperidine vinylation process (Table 1).

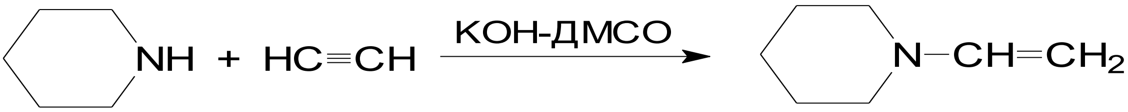
The influence of the nature of the solvent on the process during the vinylation reaction of piperidine was studied. It was observed that the solvent has a significant effect, the yield of N -vinylpiperidine without solvent was small (4.1%) . Under these conditions, the product yield in the DMSO system was equal to 19.4 %.

Table 1. Vinylation reaction of piperidine with acetylene

(reaction time 2 hours)

No	Solvent	H arorat, ^{o} S	Catalyst mi q drug KON, % (relative to piperidine mass)	N- Vinylpiperidine yield, %
1	-	55-60	10	4.1
2	DMSO	55-60	10	19.4
3	DMFA	60-65	10	14.2
4	DMFA	60-65	10+3% (ZnO)	17.1

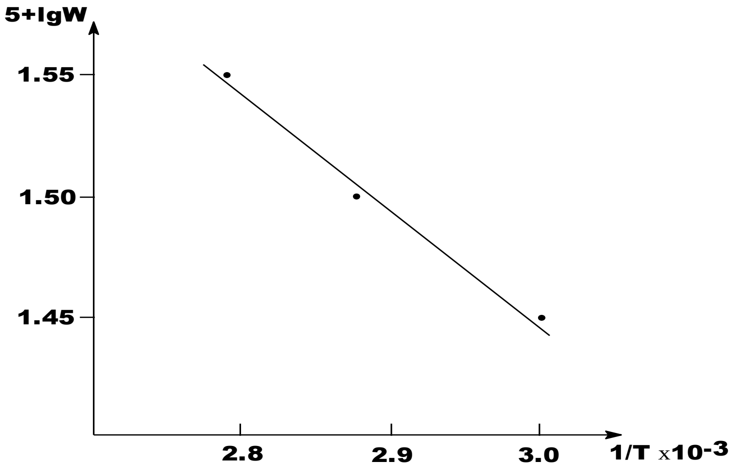
At a temperature of 60-65 ^{0} C in a DMFA solvent , the yield was 14.2 % when the amount of catalyst - KON was 10% (relative to the mass of piperidine) . In addition, the vinylation reaction of piperidine was carried out in the presence of a catalyst containing 10% KON and 3% ZnO (in relation to the mass of piperidine) . The presence of zinc oxide slightly increased the yield of N-vinylpiperidine and was equal to 17.1%. In this, the role of ZnO partially increases the solubility of acetylene. Among the solvents used in the vinylation process, DMSO was found to be relatively active. The general scheme of the reaction is as follows:



The kinetics of the reaction of piperidine with acetylene was studied (Table 2) . Based on the obtained results, the logarithm of the velocity (lgW) was plotted against the inverse temperature (1/T) (Fig. 1) and the activation energy (E) of the piperidine vinylation reaction was calculated, its value is 72.5 kJ/mol.

Table 2. Kinetic results of the piperidine vinylation process

Reaction temperature, ^{0}C	Duration of reaction, hours	N -Vinylpiperidine product		Average reaction rate (W)	
		%	mol / l	% / hour	mol / l ·s. x 10 $^{-4}$
60	1	16.4	2.18	16.4	6.05
	2	19.2	2.55	9.6	3.54
	3	23.3	3.09	7.8	2.86
	4	22.1	2.94	5.5	2.04
75	1	21.0	2.83	21.0	7.86
	2	22.3	3.00	11.1	4.17
	3	25.4	3.42	8.5	3.17
	4	23.5	3.17	5.9	2.20
85	1	24.3	3.36	24.3	9.33
	2	25.2	3.47	12.6	4.82
	3	27.0	3.72	9.0	3.44
	4	26.1	3.59	6.5	2.50
100	1	11.2	1.58	11.2	4.39
	2	9.1	1.28	4.5	1.78
	3	5.5	0.77	1.8	0.71
	4	4.8	0.68	1.2	0.47



1. Picture . Dependence of lgW on 1/T during vinylation of piperidine

The structure of N-V ynylpiperidine was confirmed by IR and PMR spectroscopic methods , and its purity was proved by YuQX and G S X.

heterogeneous-catalyzed vinylation reaction of pyridine in the presence of acetylene was carried out at atmospheric pressure. The formation of 3-vinylpyridine in the reaction is in the following scheme shown :

The influence of factors such as the nature of the solvent, the duration of the reaction, the amount of catalyst-KON and temperature on the course of the reaction was studied, and alternative conditions of the process were found: the amount of catalyst-KON was 15% (relative to the mass of pyridine), the solvent was DMSO, the temperature in the homogeneous method was 90 0 C, and in the heterogeneous method 180 ^{0}C. The yield of 3-vinylpyridine was 35.0 and 45.1%, respectively.

Based on the results obtained by vinylation of pyridine in a homogeneous way, a graph of the inverse temperature dependence of the logarithm of the rate value was drawn and the activation energy of the process was calculated, its value is 41.0 kJ/mol.

In order to compare the properties of heterocyclic amines, the vinylation reaction of morpholine was studied in highly basic systems (KON-DMSO and KON-DMFA). The reaction scheme is as follows:

In order to determine the influence of the nature and concentration of organic solvents on the vinylation reaction of morpholine, the process was carried out in the KON-DMSO system at atmospheric pressure at different reaction durations and temperatures. The activation energy of the process was calculated and its value was found to be 55.6 kJ/mol [3, 4].

In addition, the process of heterogeneous-catalytic vinylization of morpholine was also studied. 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 alternative temperature in the gas phase was 250-255 ^{0}C, and the product yield was 31.7%.

Based on the results of laboratory experiments on vinylization of morpholine, a catalyst based on activated carbon and potassium hydroxide was produced at the experimental facility of UzKFITI named after A. Sultonov, and it was used for the synthesis of N-vinylmorpholine in the enlarged facility. It was found that the KON/activated carbon catalyst has sufficient activity in the heterogeneous-catalytic vinylation reaction of morpholine, and it was recommended to be used in practice.

REFERENCES

1. Trofimov B.A. Reaction of acetylene in superbasic media // Uspekhi khimii, 1981, T.50. Issue 2. P.250-255.
2. Trofimov B.A., Nesterenko R.N., Mikhaleva A.I. New examples of vinylation of NH-heterocycles with acetylene in the KOH-DMSO system // KhGS. -Riga, 1986, -No. 4, -P.481-485.
3. Nurmanov S.E., Alibekova R.A., Mirkhamitova D.Kh. Catalytic synthesis of N-vinylmorpholine // Science and education of Southern Kazakhstan. Series chemistry, chemical technology. -Kazakhstan, 2003, -No. 35, -P.41-43.
4. Mirkhamitova D.Kh., Nurmanov S.E., Rashidova S.Sh. Synthesis of N-vinylmorpholine by homogeneous and heterogeneous methods // Bulletin of NUUz. -Tashkent, 2005, -No. 4, -P.52-54.

ISSN 2576-5973 (online), Published by "Global Research Network LLC"
under Volume: 6 Issue: 10 in Oct-2023 https://globalresearchnetwork.us/index.php/ajebm