CATALYTIC SYNTHESIS OF PYRIDINE AND METHYLPYRIDINE FROM ACETYLENE AND AMMONIA

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A method was developed for the preparation of pyridine and methylpyridines by ammonolysis of acetylene in the presence of cadmium phosphate. The ratio of the final products depends primarily on the reaction temperature. The formation of pyridine and methylpyridines proceeds through a number of intermediate steps.

An extremely promising method for the preparation of pyridine and methylpyridines is their synthesis from acetylene and ammonia in the presence of catalysts [1-4]. However, the effect of a number of factors – the composition and properties of the catalyst, the synthetic temperature, the volume ratio of acetylene and ammonia, and their overall space velocity – has not been investigated. Of the available papers, the problem of the reaction mechanism is touched upon in only a few, but the opinions of the authors on this problem are contradictory and in some cases absolutely inexplicable.

In the present research we studied the reaction of acetylene with ammonia in order to obtain pyridine and picolines in the presence of heterogeneous catalysts. In choosing the catalyst we proceeded from assumptions that the catalyst should be capable of activation not only of acetylene but also of the molecule added to it [5], in this case ammonia. A comparison of the catalytic properties of oxides, phosphates, and salts of group II metals, which have the capacity to complex with acetylene and ammonia, showed that the indicated requirements are met by cadmium phosphate, which can be used in the form of granules or on a support with a neutral surface. It is known that cadmium phosphate is used as a catalyst, for example, in the preparation of acetaldehyde, the hydration of acetylene [6], and the ammonolysis of the latter in order to obtain pyridine bases [7].

The experimental studies showed that the ratio of the reaction products depends primarily on the reaction temperature. The optimum temperature for the synthesis of 2- and 4-methylpyridines ranges from 420 to 440° C (Fig. 1). The optimum space velocity with respect to acetylene is 100 liters/liter·catalyst·h, and the optimum $NH_3 : C_2H_2$ molar ratio is 2:1 (Figs. 2 and 3). Under the optimum conditions, the yield of 2-methylpyridine is 56.3 wt. %, the yield of 4-methylpyridine is 31.4 wt. % with respect to the catalyzate, and the acetylene conversion is 65-80 %.

In order to obtain pyridine and 3-methylpyridine, methanol was fed into the zone of contact between acetylene and ammonia. The optimum temperature for the synthesis of pyridine and methylpyridine is 420° (Table 1). The ratio of the reaction products depends on the relative amount of methanol in the reaction mixture fed into the contact zone (Table 2). An increase in the amount of methanol in the mixture raises the yield of 3-methylpyridine.

The results make it possible to make some assumptions regarding the mechanism of the formation of pyridine and its monomethyl homologs. It is known that, despite Chichibabin's assumption [1], the presence of water [8] is not compulsory for the formation of pyridine bases from acetylene and ammonia. We

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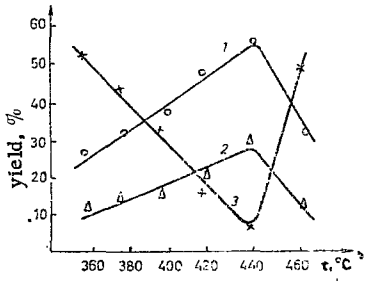


Fig. 1

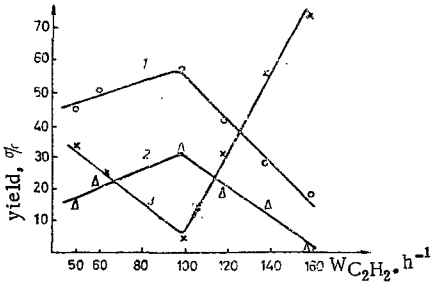


Fig. 2

Fig. 1. Effect of the temperature on the yields of α- and γ-picolines (C_2H_2 = 100 liters/liter · catalyst · h, NH_3/C_2H_2 = 2): 1) α-picoline; 2) γ-picoline; 3) acetonitrile.

Fig. 2. Effect of the space velocity on the yields of α- and γ-picolines (420° C, NH_3/C_2H_2 = 2): 1) α-picoline; 2) γ-picoline; 3) acetonitrile.

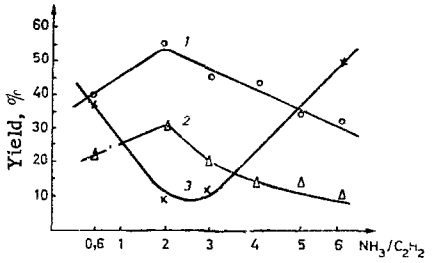
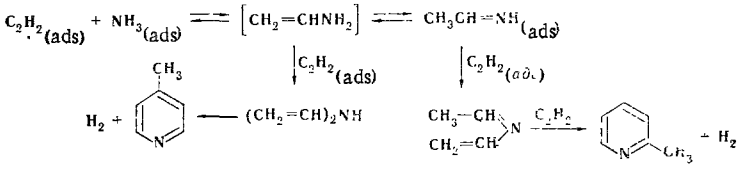


Fig. 3. Effect of the volume ratio of acetylene and ammonia on the yields of α- and and γ-picolines (420° C, $W_{C_2H_2}$ = 100 liters/liter · catalyst · h: 1) α-picoline; 2) γ-picoline; 3) acetonitrile.

have established that in the presence of water vapor the ammonolysis of acetylene is directed to favor the formation of acetonitrile with a reduction in the yield of the pyridine bases. The formation of pyridine bases through a step involving acetonitrile [4] also seems unlikely. We propose a scheme for the formation of pyridine bases from acetylene and ammonia in which the latter are adsorbed on the catalyst surface and interact to form vinylamine or ethylenediamine, which react further with a new molecule of acetylene to give di(vinyl)amine. The formation of a di(vinyl)amine is confirmed by the fact that diethylamine – the product of hydrogenation of di(vinyl)amine [9] – is detected in the reaction products when cadmium, zinc, or iron salts are present. The case of monoethanolamine, which gives the same pyridine bases when it is passed with acetylene through a catalyst under the conditions of the indicated reaction, may serve as another proof in favor of the formation of di(vinyl)amine. Di(vinyl)amine, by reacting with another molecule of acetylene and undergoing rearrangement, is converted to 2- and 4-methylpyridines.



In regards to the formation of pyridine and β-picoline in the presence of methanol, on the basis of the established dependence of the yields of these compounds on the amount of methanol it might be assumed that they were formed as a result of the reaction of di(vinyl)amine with methanol rather than with acetylene. In this case, the intermediate necessary for the formation of pyridine is obtained when the reagent ratio is equimolecular, whereas 2 moles of methanol per mole of di(vinyl)amine are necessary for the production of β-picoline. No data whatsoever on the mechanism of the formation of pyridine and β-picoline from the above-indicated products are available in the literature.

EXPERIMENTAL

The catalyst was prepared by coprecipitation from trisubstituted ammonium phosphate, cadmium nitrate, and bentonite (the support). The appropriate amounts of the above-indicated cmopounds based on 20 wt. % cadmium phosphate were mixed in bulk and stirred for 30 min. After this, the resulting precipitate was removed by filtration, washed, and dried at 105-120° for 3 h. Pellets (4 × 2 mm) were prepared from the resulting mass and calcined thoroughly at 450-500° for 3 h. The resulting catalyst had a specific area (S_{sp}) of 132 m^2/g.

TABLE 1. Dependence of the Yields of Pyridine and Picolines on the Temperature ($W_{C_2H_2}$ = 100 liters/liter · catalyst · h, $C_2H_2-NH_3-CH_3OH$ = 1 : 1 : 1)

Temp., °C	Pyridine, %	α-Picoline, %	β-Picoline, %
380	15,0	14,5	0,0
400	18,3	21,6	Traces
420	27,0	22,0	9,0
440	17,6	15,2	8,0

TABLE 2. Dependence of the Yield of Pyridine and Picolines on the Relative Amount of Methanol (420° C, W_{tot} = 200 liters/liter · catalyst · h, $C_2H_2 : NH_3$ = 1 : 1)

Amount of methanol in the mixture, mole	Percentages of the bases, %			
	pyridine	α-picoline	β-picoline	γ-picoline
0,0	0,0	56,3	0,0	31,4
0,5	14,5	23,2	7,1	Traces
1,0	27,0	22,0	9,1	0,0
1,5	10,2	7,9	12,3	0,0
2,0	6,2	Traces	14,5	0,0

The catalytic condensation of acetylene with ammonia was carried out in a flow apparatus. The temperature, space velocities, ratio of acetylene to ammonia, and the partial pressures of the starting components (by dilution with nitrogen and water vapors) were varied. In all cases, the experiment was begun after establishment of steady-state conditions, and this was verified by analysis of the products at the outlet from the reactor with time.

The acetylene and ammonia were subjected to preliminary purification and drying with calcium chloride and dry potassium hydroxide by the method in [10]. The reaction products were analyzed by gas–liquid chromatography (GLC) with an LKhM-7A chromatograph; the stationary phase was 17-20 % polyethylene glycol adipate on Cellite-545, the column length was 2 m and its diameter was 4 mm, the column temperature was 140°, and the helium flow rate was 50 ml/min. The retention time of 2-methylpyridine was 114 sec, as compared with 145 sec for 4-methylpyridine. The exhaust gases consisted primarily of hydrogen and unchanged acetylene. The individual reaction products were isolated by fractionation of the catalyzate in a column with 30 theoretical plates. The pyridine bases were identified from their IR spectra and the properties of their picrates.

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LITERATURE CITED

1. A. E. Chichibabin, Zh. Russk. Fiz.-Khim. Obshchestva, 47, 703 (1915).
2. K. K. Moll, Chem. Techn., 19, 528 (1967).
3. F. Sailak and V. Veler, US Patent No. 2807618 (1957); Ref. Zh. Khim., 72234 (1959).
4. E. V. Lukin, A. P. Musakin, G. N. Nikandrov, and G. N. Semanov, Zh. Prikl. Khim., 42, 2109 (1969).
5. R. M. Flid, Zh. Fiz. Khim., 32, 2339 (1958); Kinetika i Kataliz, 2, 66 (1961).
6. Yu. A. Gorin, Zh. Obshch. Khim., 28, 1144, 2338 (1958).
7. T. Isiguro, Japanese Patent No. 7319 (1954); Ref. Zh. Khim., 61694P (1957).
8. J. Dewar, Jahresber. der Chemie, 445 (1877).
9. German Patent No. 479351 (1929); Chem. Zentralblatt, 2, 2575 (1930).
10. K. M. Akhmerov, Master's Dissertation, MITKht, Moscow (1966).