VAPOR-PHASE CATALYTIC OXIDATION OF A β-PICOLINE FRACTION

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The vapor-phase catalytic oxidation with atmospheric oxidation of a β-picoline fraction consisting of a mixture of 3- and 4-methylpyridines and 2, 6-lutidine containing small amounts of 2-methylpyridine and pyridine has been studied. On a vanadium oxide catalyst at 440° C with a contact time of 1.2 sec and a molar ratio of oxygen to steam to methylpyridine of 7 : 54 : 1, a high degree of conversion of the 4-methylpyridine and the 2, 6-lutidine into pyridine-4-aldehyde and 6-methylpyridine-2-aldehyde, respectively, has been achieved. The main component of the aqueous solution of the catalyzate (after the isolation of the pyridine aldehydes in the form of oximes) is 3-methylpyridine.

In a preceding paper [1] we gave the results of a study of the vapor-phase oxidation of the individual methylpyridines and showed that under the conditions that are optimum for the oxidation of 2- and 4-methylpyridines to pyridine aldehydes the conversion of 3-methylpyridine is extremely low. It appeared of interest to carry out the oxidation of a β-picoline fraction under conditions ensuring the maximum conversion of the 4-methylpyridine into the corresponding aldehyde and the simultaneous enrichment of the mixture of pyridine bases with 3-methylpyridine. Some time ago, the vapor-phase oxidation of a β-picoline fraction in order to enrich it in 3-picoline was carried out by I. M. Polyakova [2]. She selected conditions under which the methylpyridines accompanying the 3-methylpyridine in the β-fraction underwent complete combustion.

Other authors have also dealt with the oxidation of a β-picoline fraction [3–5]. But they pursued the aim of the selective oxidation of the 4-methylpyridine contained in this fraction to isonicotinic acid and were not interested in the reactions of the other components.

Under the conditions of the vapor-phase oxidation of the β-picoline fraction in the presence of steam, the formation of considerable amounts of pyridine aldehydes (up to 44% calculated on the whole fraction) takes place, the yield of enriched fraction amounting to 25–66% according to the excess of oxygen and the time of contact (Table 1). Pyridinecarboxylic acids and products of complete combustion are formed in comparatively small amounts. When the excess of oxygen in the mixture is increased to a molar ratio of oxygen to picoline of 16, with a time of contact of 1 sec or more, the amount of complete oxidation increases considerably. With a contact time of 1.2 sec and a molar ratio of oxygen to picoline of 7, it is possible to raise the content of 3-methylpyridine in the picoline fraction to 73% with no change whatever in its absolute amount (Table 2). Simultaneously the amounts of 2-methylpyridine and pyridine in the catalysate increase. But, on passing to more severe conditions (the last two experiments), the amount of 2-methylpyridine begins to fall. The most stable compound under these conditions is pyridine, the amount of which rises by a factor of more than 3. Under these conditions the 4-methylpyridine is converted into the pyridine aldehyde.

As follows from Table 3, the yields of pyridine-4-aldehyde are almost the same as in the oxidation of pure 4-methylpyridine under the optimum conditions.

It follows from a comparison of the conversions of 4-picoline and 2, 6-lutidine (Table 3) that their reactivities are fairly similar. The main product of the oxidation of 2, 6-lutidine is 2, 6-methylpyridine-2-aldehyde, the yield of which amounts to 91.0%. 2, 6-Lutidine is also converted into 2-methylpyridine and further, obviously, into pyridine. The high yield of 6-methylpyridine-2-aldehyde can be explained by the high stability of this compound under the reaction conditions.

Thus, the vapor-phase catalytic oxidation of the β-picoline fraction on vanadium catalysts at 440° C with a low concentration of oxygen in a reaction mixture diluted with steam leads to an enrichment of the fraction with 3-methylpyridine and simultaneously permits difficultly accessible pyridine aldehydes to be obtained.

The enriched β-picoline fraction can be used without additional purification for the production of nicotinic acid.

EXPERIMENTAL

The experiments were carried out with a β-picoline fraction having bp 143–145° C, n_D^{20} 1.5048, d_4^{20} 0.89223, containing 24.6% of 2, 6-

Table 1

Composition of the Reaction Products as Functions of the Time of Contact and the Amount of Oxygen (Temperature 440° C; molar ratio of air to picoline = 54)

Time of contact, sec	Molar ratio of oxygen to picoline	Yield of enriched fraction, %	Total yield of aldehydes, %	Yield of acid, %	Products of complete combustion, %
0.36	8.0	66.2	19.5	2.4	5.8
0.50	8.3	61.0	22.5	2.7	8.3
0.58	10.4	47.8	32.7	3.1	9.4
1.10	5.7	56.7	31.5	1.7	7.2
1.20	7.0	44.5	44.5	2.2	10.9
1.15	16.4	25.4	34.0	4.6	21.3

Table 2

Change in the Composition of the Picoline Fraction as a Result of the Catalytic Reaction

Picoline fraction recovered, %		Pyridine bases, %					
		3-picoline	4-picoline	2,6-lutidine	2-picoline	pyridine	unidentified bases
100	I*	31.5	34.5	24.6	5.7	1.2	2.5
66.2	I	45.7	15.2	17.4	15.5	6.2	—
	II	96.0	29.0	46.7	178.0	341.0	—
61.0	I	46.6	16.3	12.8	16.7	7.7	—
	II	90.0	28.7	31.7	177.0	391.0	—
47.8	I	48.9	16.5	8.9	17.7	8.0	—
	II	94.4	22.8	17.4	147.0	316.0	—
56.7	I	63.7	10.7	6.4	10.1	10.1	—
	II	111.4	17.5	12.4	100.0	475.0	—
44.5	I	73.3	4.4	4.2	5.7	12.4	—
	II	103.0	5.6	7.5	44.0	457.0	—
25.4	I	76.3	3.8	1.4	5.7	12.8	—
	II	60.5	2.8	1.5	25.3	270.0	—

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*I—content of pyridine bases in the catalysate; II—change in the absolute amount of pyridine bases in relation to the initial fraction in %.

Table 3

Conversion of the Individual Components of the Fraction*

4-Picoline		2,6-Lutidine		
conversion into aldehyde, %	total conversion %	conversion into aldehyde, %	conversion into 2-picoline, %	total conversion %
42.0	71.0	10.6	21.0	53.3
43.0	71.3	23.8	20.5	68.3
48.0	77.2	52.0	12.6	82.6
37.0	82.5	60.0	—**	87.6
56.0	94.4	81.0	—	92.5
22.0	97.2	91.0	—	98.5

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* For experimental conditions, see Table 1.

** It is impossible to determine the degree of conversion of the 2,6-lutidine into 2-picoline under the given conditions because of the further reactions of the 2-picoline.

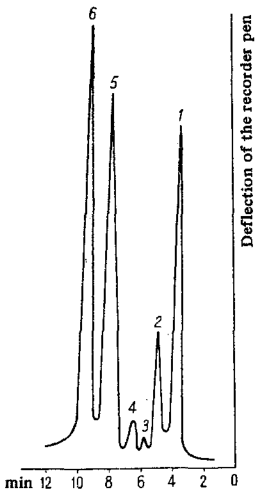

Fig. 1. Chromatogram of the β-picoline fraction: (1) 2,6-dimethylpyridine; (2) 2-methylpyridine; (3) pyridine; (4) unidentified bases; (5) 3-methylpyridine; (6) 4-methylpyridine.

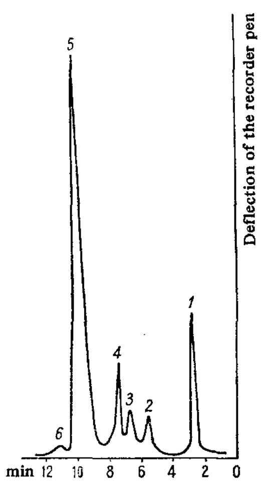

Fig. 2. Chromatogram of the picoline fraction of the catalysate: (1) ethanol; (2) 2,6-dimethylpyridine; (3) 2-methylpyridine; (4) pyridine; (5) 3-methylpyridine; (6) 4-methylpyridine.

lutidine, 31.5% of 3-methylpyridine, 34.5% of 4-methylpyridine, 5.7% of 2-methylpyridine, 1.2% of pyridine, and 2.5% of unidentified bases.

Oxidation was carried out in a laboratory-type continuous apparatus. The catalyst, which consisted of oxides of vanadium, molybdenum, titanium, and phosphorus deposited on metallic aluminum, has been described previously [6].

The compositions of the initial fraction and the catalyzate (Figs. 1 and 2) were determined by gas-liquid chromatography on a Khrom-1 chromatograph with a flame ionization detector. The chromatographic columns, 3 m long, were filled with Celite 545 impregnated with 30% of glycerol, and were thermostated at 120° C.

The quantitative determination of the pyridine aldehydes was carried out polarographically in the presence of an acetate buffer (pH 5.5). The sum of the pyridine-2- and -4-aldehydes was calculated from the polarographic wave with $E_{1/2}$ 0.7 V, and the amount of 6-methylpyridine-2-aldehyde from the wave with $E_{1/2}$ 0.95 V.

For identification, the aldehydes were precipitated from the catalyzate in the form of a mixture of oximes.

The oximes of the individual aldehydes were separated by fractional crystallization from 25% ethanol: pyridine-4-aldehyde oxime—crystalline substance with mp 129–130° C (130–132° C [7]). Found, %: C 59.60; H 4.91; N 22.64. Calculated for ($C_6H_6N_2O$), %: C 59.02; H 4.92; N 22.95; 6-methylpyridine-2-aldehyde oxime—white crystalline substance with mp 168–170° C (170–171° C [7]). Found, %: C 61.63; H 6.47; N 19.84. Calculated for ($C_7H_9N_2O$), %: C 61.31; H 6.57; N 20.44.

Pyridine-2-aldehyde is formed in very small amounts, and the corresponding oxime could not be isolated from the catalysate.

The total content of pyridinecarboxylic acids in the catalysate was determined by alkalimetric titration.

The gaseous products of complete combustion were analyzed on a VTI-2 gas analyzer.

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