REACTIVITY OF METHYLPYRIDINES IN VAPOR-PHASE CATALYTIC OXIDATION

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 1061–1065, 1968

UDC 547.821.411:541.127:542:943.7

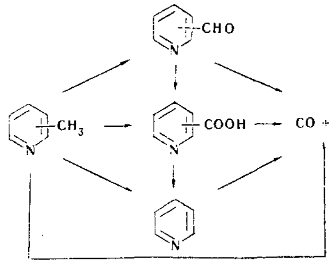
The reactivity of 2-, 3-, and 4-methylpyridines in vapor-phase catalytic oxidation was studied over a vanadium–molybdenum–phosphorus catalyst, deposited on fine-pored corundum (in nongradient conditions). The rate of total conversion of the methylpyridines decreases in the following series: 4-methylpyridine > 2-methylpyridine > > 3-methylpyridine. It is suggested that scission of the C–H bond in the methyl group of the oxidized compound is the first step in the process.

In previous papers [1,2] devoted to the choice of selective catalysts and optimum conditions of oxidation of 2-, 3-, and 4-methylpyridines to pyridine aldehydes it was shown that the degree of conversion and the quantitative ratios of the products vary in dependence on the position of the methyl group in relation to the heteroatom, provided that the reactions are carried out in comparable conditions.

The present work describes the results of studying the comparative reactivity of 2-, 3-, and 4-methylpyridines.

In the experimental conditions selected, the reaction proved highly nonselective. Products of complete oxidation were formed in significant yield together with products of the mild oxidative degradation of the picolines.

By analogy with other vapor-phase catalytic processes for hydrocarbon oxidation [10–13], it may be assumed that the reaction products mentioned are formed by a parallel-consecutive mechanism according to the scheme:



However, no kinetic data for this scheme are given.

The rate of total conversion of methylpyridines (W_{tot}) decreases in the following sequence (Table 1): 4-methylpyridine > 2-methylpyridine > 3-methylpyridine.

The value of W_{tot} for the oxidation of 2-methylpyridine is somewhat lower than that for 4-methylpyridine, while that for 3-methylpyridine is four times lower.

Direction of the reaction also varies according to the nature of the component undergoing oxidation. While oxidation of 2-methylpyridine affords the pyridinealdehyde as the main product of partial oxidation, the reaction of 4-methylpyridine goes in the direction of the formation of a product of the further oxidation of the methyl group—4-pyridinecarboxylic acid (the maximum selectivity of formation of 4-pyridinecarboxylic acid is 25%) (Table 2).

With a large excess of oxygen in the reaction mixture and slight dilution with steam, the rate of accumulation of 4-pyridinealdehyde is an order of magnitude below that of 2-pyridinealdehyde. In these conditions, this may be explained by the high rate of the succeeding conversion reaction of 4-pyridinealdehyde.

The important role of the processes leading to the further oxidation of the primary partial-oxidation products of 2- and 4-methylpyridines is shown by data on the dependence of the selectivity of the process on the linear velocity of the reaction mixture. An increase in the space velocity from 7300 to 24 000 hr^{-1} causes a twofold increase in the selectivity of the formation of 2- and 4-pyridinealdehydes. Meanwhile a simultaneous lowering of the W_{CO+CO_2}/W_{tot} ratio occurs. The latter supports the hypothesis that, under the experimental conditions selected, the further oxidation of the pyridinealdehydes and, apparently, of the pyridinecarboxylic acids and pyridine has a substantial influence on the course of the process.

A considerable quantity of pyridine is formed in the oxidation of the methylpyridines. Rate of formation of pyridine falls symbatically with the lowering of the rate of formation of pyridinecarboxylic acids. Maximum selectivities of pyridine formation in the oxidation of 2- and 4-methylpyridines are 36 and 20%, respectively.

Condensation products are formed in considerable amounts in the oxidation of 4-methylpyridine (rate—21×10^{-5}–63×10^{-5} mole/$m^2 \cdot$ hr, selectivity 3–11%), while the oxidation of 2-methylpyridine under the specified conditions affords only traces of 2,2'-pyridoin in the catalyzates (the selectivity does not exceed 2%).

As in the case of the total conversion reaction of the methylpyridines and that of the formation of pyridine, the rate of formation of carbon monoxide and carbon dioxide falls in the sequence (Table 1) 4-methylpyridine > 2-methylpyridine > 3-methylpyridine.

The rate of formation of carbon monoxide and carbon dioxide (W_{CO+CO_2}) for the oxidation of 2-methylpyridine is somewhat lower than the corresponding value for the oxidation of 4-methylpyridine. In vapor-phase catalytic oxidation of 3-methylpyridine, this value falls by a factor of 2–3.

The selectivity of formation of the total products of partial oxidation and of oxidative dealkylation is highest in the oxidation of 4-methylpyridine, and lowest in the oxidation of 3-methylpyridine. (The value of the ratio

Table 1

Influence of Structure of the Picoline Oxidized on the Rate of Total Conversion and of the Formation of Aldehydes, Acids, Pyridine, and Condensation and Highly Oxidized Products at 430° C*

Component oxidized	$C \cdot 10^5$, mole/l	V, hr^{-1}	$W_{tot} \cdot 10^5$, mole/m² · hr	$W_a \cdot 10^5$, mole/m² · hr	$W_c \cdot 10^5$, mole/m² · hr	$W_p \cdot 10^5$, mole/m² · hr	$W_d \cdot 10^5$, mole/m² · hr	$W_{CO+CO_2} \cdot 10^5$, mole/m² · hr
2-Methylpyridine	42.20	23900	567.0	136.10	33.30	146.00	7.35	221.7
	32.00	14300	442.0	102.30	28.50	109.60	6.00	215.0
	24.72	9900	324.5	56.23	20.89	74.13	5.32	181.6
3-Methylpyridine	64.8	23900	161.0	16.22	9.68	9.75	—	86.6
	59.4	10000	117.0	14.86	9.61	9.14	—	81.6
	48.3	6540	106.3	13.09	9.36	8.36	—	76.3
4-Methylpyridine	48.4	23900	705.0	13.49	171.4	128.5	62.8	311.6
	41.11	14350	646.0	11.75	169.8	119.9	53.7	238.3
	25.12	9890	489.0	7.08	128.8	100.0	20.5	221.6

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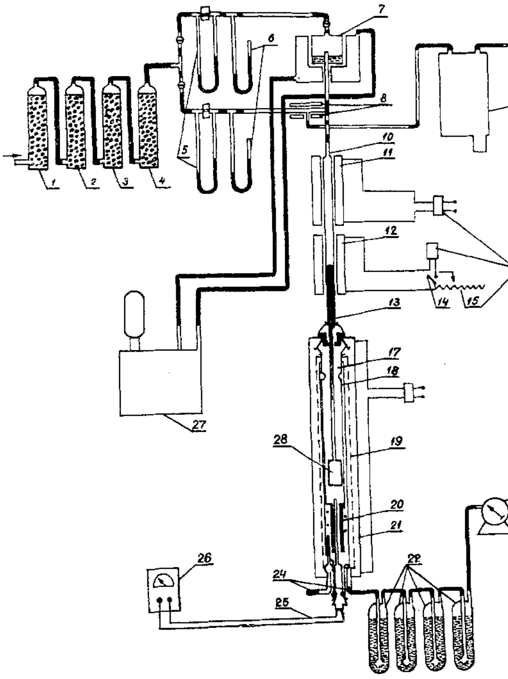
*W_a, W_c, W_p, W_d, W_{CO+CO_2}, and W_{tot}–rates of formation of aldehyde, pyridinecarboxylic acid, pyridine, condensation products, products of complete oxidation and complete conversion, respectively.

Table 2

Variation of the Selectivity of the Oxidation of 2-, 3-, and 4-Methylpyridines with Space Velocity

Component oxidized	Temp., °C	V, hr^{-1}	$\frac{W_a}{W_{tot}} \cdot 100$, %	$\frac{W_c}{W_{tot}} \cdot 100$, %	$\frac{W_p}{W_{tot}} \cdot 100$, %	$\frac{W_d}{W_{tot}} \cdot 100$, %	$\frac{W_{CO+CO_2}}{W_{tot}} \cdot 100$, %
2-Methylpyridine	400	7280	12.7	5.0	16.5	1,50	64.0
	400	23900	33.3	6.4	35.5	1.43	23.2
	430	9900	17.4	6.4	22.8	1.60	56.0
	430	23900	24.0	5.9	25.8	1.30	39.0
3-Methylpyridine	400	6420	13.8	14.6	8.6	0.12	74.0
	400	23800	11.1	8.6	5.8	0.10	62.0
	430	6540	12.3	8.8	7.8	1.0	72.0
	430	23900	10.1	6.0	6.1	1.10	53.8
4-Methylpyridine	400	7280	1.2	22.0	15.8	4.2	57.0
	400	23900	2.5	25.0	16.9	10.9	44.5
	430	7310	0.94	23.0	19.8	3.4	52.6
	430	23900	1.9	24.3	18.2	8.9	44.1

W_{CO+CO_2}/W_{tot} in the oxidation of 3-methylpyridine is 0.54–0.7 and in the oxidation of 4-methylpyridine it does not exceed 0.57).



Apparatus with continuous circulation: 1) column of carbon, 2) calcium chloride, 3) soda lime, 4) Ascarite, 5) flowmeters, 6) manometers, 7) thermostated surface carburetor, 8) steam generator, 9) metering pump, 10) gas inlet, 11) superheater, 12) electromagnetic coil, 13) chamber with strips of transformer iron, 14) switch, 15) rheostats, 16) laboratory autotransformers, 17) inner reactor chamber, 18) outer reactor chamber, 19) wire of the heating element, 20) catalyst chamber, 21) glass cylinder, 22) absorbers, 23) drum-type gas meter, 24) outlet for reactor gases, 25) thermocouple, 26) K-59 potentiometer, 27) thermostat, 28) glass piston.

The apparent activation energies for the oxidation of 2-, 3-, and 4-methylpyridines (Table 3) were found from the variations with temperature of the over-all rates of conversion of the methylpyridines. The apparent activation energy values found also agree with the sequence of reactivities given above and with basicities of the methylpyridines [14].

It is important to note that the highest reactivity is found with 4-methylpyridine, and the lowest with 3-methylpyridine, also in such conversion reactions as deutero-exchange [15], conversion dealkylation [16], and condensation [17].

It is possible to assume that there may be common stages in reactions connected with the conversion of methyl groups in various hydrocarbons and in pyridine derivatives. In the production of pyridinealdehydes by the vapor-phase catalytic oxidation of methylpyridines, the first, and perhaps in some cases the limiting, stage is C—H bond scission in the methyl group.

This mechanism has been proposed for the demethylation reaction on nickel catalysts, the pyrolysis of methylpyridines and toluene [18], and the contact vapor-phase oxidation of hydrocarbons on copper catalysts [19].

On the other hand, we have found frequency shifts of 43 cm^{-1} for the wagging vibrations of the CH_3 group in the IR spectrum of 2-methylpyridine, adsorbed on a vanadium catalyst which can obviously be explained by the chemisorption of the methylpyridine at the methyl group. In this case, it is possible that some weakening of the C—H bond occurs [20].

EXPERIMENTAL

The experiments were conducted in a nongradient reactor designed by G. P. Korneichuk [3]. (The general plan of the apparatus is shown in Fig. 1). The initial concentration of methylpyridine in the steam-air mixture was 54–61 × 10^{-5} mole/l and the temperature was 370–430° C. The dilution of the reaction mixture with air and steam corresponded to an oxygen-water-methylpyridine molar ratio of 12–13: 10: 1.

In order to decrease the influence of macrokinetic factors on the velocity of the process, the active components—oxides of vanadium, molybdenum, phosphorus, sodium, and nickel (1% of the weight of the catalyst)—were deposited on low-porosity corundum having practically zero internal surface area (S_{spec} = 0.003 m^2/g, porosity 3–7%). The specific surface was determined by the BET method using the low-temperature absorption of krypton. The porosity of the carrier was determined by the mercury penetration method. The vanadium–molybdenum–phosphorus cataryst had a specific surface of 0.34 m^2/g and a bulk density of 2.0 g/cm^3 [4].

The oxidation reaction of the methylpyridines afforded the corresponding pyridinealdehydes and pyridinecarboxylic acids, pyridine, products of far-reaching conversion, and condensation products of pyridinealdehydes–2, 2'-pyridoin (from the oxidation of 2-methylpyridine) and 1, 2-di(4'-pyridyl)-1, 2-ethanediol (from the oxidation of 4-methylpyridine).

A polarographic method [5–7] was used for the quantitative determination of the pyridinealdehydes, the 2, 2'-pyridoin, and the pyridinecarboxylic acids. The catalyzates were analyzed in acetate buffer at pH 5.5 on a TsPE-312 electronic recording polarograph.

In parallel, the pyridinecarboxylic acids were titrated with 0.01 N alkali to phenolphthalein. 1, 2-Di(4'-pyridyl)-1, 2-ethanediol was determined by iodometric titration [6].

Purity of the initial methylpyridines and of the pyridine formed and of the unchanged methylpyridines was determined on a Khrom-1 gas-liquid chromatograph (stationary phase—Apiezon M, 20–25% on Chromosorb W). Carbon monoxide and dioxide were determined by a published method [9].

Table 3

Comparision of Apparent Activation Energies for Over-all Conversion and Basicities of the Methylpyridines.

Compound oxidized	pK_a[14]	E, kcal/mole
4-Methylpyridine	6.025	10.0
2-Methylpyridine	5.943	13.0
3-Methylpyridine	5.657	18.0

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19 December 1966

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