

## VAPOR PHASE OXIDATION OF METHYLPYRIDINE ALDEHYDES

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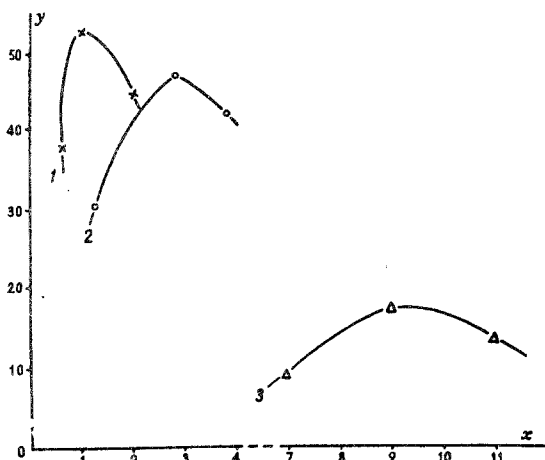
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A study is made of the contact oxidation of  $\alpha$ -,  $\beta$ - and  $\gamma$ -methylpyridines by air, over the temperature range 390°-490° C, contact time 0.17-1.0 sec, mole ratio oxygen:methylpyridine 0.5 to 40:1, with dilution of the air-vapor mixture with water in the ratio 15-103 mole water per mole methylpyridine, using two vanadium oxide catalysts differing in respect of sizes of specific surface areas. Use of the low specific surface area catalyst increases the selectivity of the process, by diminishing the proportion of secondary reaction products of the aldehydes and decreasing the complete oxidation of the methylpyridines.

The literature contains isolated papers on the oxidation of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -methylpyridines by aerial oxygen over vanadium oxide catalysts [1, 2]. The corresponding aldehydes are obtained when the reaction mixture is diluted with steam, yields being greater or lesser, depending on the starting material and on the catalyst used.

The oxidation of  $\alpha$ -methylpyridine gives, along with the aldehyde, a considerable amount of pyridine and pyridone derived from the aldehyde, and some pyridinecarboxylic acid. It was of interest to know the behaviors of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -methylpyridines over vanadium oxide catalysts under comparable conditions. In our previous work on the oxidation of  $\alpha$ -methylpyridine using vanadium oxide catalyst supported on silica, specific surface area 18.06 m<sup>2</sup>/g, temperature 425° C, contact time 0.30 sec, oxygen:water:picoline mole ratios 0.9:36:1, the yield of  $\alpha$ -pyridine aldehyde was 60% theory, and of pyridone 10.5%, with 99% pyridine conversion [1].



Oxidation of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -methylpyridines at 435°-440° C ( $\tau = 0.3-0.4$  sec). y) Yield of pyridinaldehyde, %; x) mole ratio oxygen:methylpyridine; 1)  $\alpha$ -pyridinaldehyde; 2)  $\gamma$ -pyridinaldehyde; 3)  $\beta$ -pyridinaldehyde.

The present paper sets out the results of research on oxidation of methylpyridines over two vanadium oxide catalysts differing in respect of specific surface area, and gives the optimum oxidation conditions for each of the isomers.

Table 1  
Physicochemical Properties of Starting Isomeric Methylpyridines

Iso-mer	Bp, °C at 760 mm	$n_D^{20}$	$d_4^{20}$
$\alpha$ -	128	1.5010	0.9443
$\beta$ -	142-144	1.5035	0.9560
$\gamma$ -	142-145	1.5058	0.9547

Because of different electron densities at the methyl carbon atom with  $\alpha$ -,  $\beta$ - and  $\gamma$ -methylpyridines, they are converted to different extents under the conditions of the vapor phase contact reaction. Oxidation of  $\beta$ -methylpyridine takes place under much more drastic conditions, than are required for  $\alpha$ - and  $\gamma$ -methylpyridines.

While at 430°, contact time 0.35 sec, and mole ratio oxygen:methylpyridine 1:1, the yield of  $\alpha$ -pyridinaldehyde is 53%, the yield of  $\gamma$ -pyridinaldehyde under the same conditions is only 20%, while practically no  $\beta$ -pyridinaldehyde is formed.

The maximum yields of  $\alpha$ -,  $\gamma$ -, and  $\beta$ -pyridinaldehydes, 53.6, 47.2, and 17.1%, or 60.0, 55.0, and 44.0% theory, are obtained at a mole ratio oxygen:methylpyridine 0.9, 3, and 9:1, respectively (figure).

A similar relationship was found [6] in the oxidation of picolines to pyridinecarboxylic acids. The best yield of  $\alpha$ -pyridinecarboxylic acid, 18.8%, was obtained at an oxygen:picoline ratio of 9, while the best yield of  $\gamma$ -pyridinecarboxylic acid, 11%, was obtained when the ratio was 12.

Comparison of yields of pyridinaldehydes, calculated on unreacted methylpyridine, shows that despite considerable increase in the concentration of oxygen in the reaction mixture, over 50% of the  $\beta$ -methylpyridine is unoxidized, whereas  $\alpha$ - and  $\gamma$ -methylpyridines react almost completely at oxygen concentrations which are 3 and 9 times less.

The oxidation products from the methylpyridines contain, in addition to pyridinaldehydes, pyridine, pyridinecarboxylic acids, and in the cases of the  $\alpha$  and  $\gamma$  isomers, dimerization products.

The yields of pyridine, on passing from the  $\alpha$  to the  $\beta$ , and to the  $\gamma$  isomer vary similarly to the yields of aldehydes. The highest yield of pyridine,

Table 2  
 Yields of Oxidation Products of  $\beta$ - and  $\gamma$ -Methylpyridines over the High Specific Surface Area Catalyst\*

Temperature °C	Contact time, sec	Oxygen:picoline mole ratio	Water:picoline mole ratio	Yield, %			
				Pyridinaldehyde		Pyridin- carboxylic acid	Pyridine
				On picoline passed	On picoline reacted		
$\gamma$ -Methylpyridine							
350	0.20	1.9	54.0	35.2	50.0	not determined	not determined
390	0.40	1.6	76.2	16.1	52	0.6	1.6
410	0.20	3.2	32.0	21.9	36.0	1.7	not determined
410	0.40	1.9	76.2	18.4	not determined	not determined	not determined
410	0.50	1.6	76.2	20.2	not determined	not determined	not determined
420	0.35	2.8	54.0	47.2	55.0	10.0	4.0
420	0.40	2.0	54.0	38.2	52.0	not determined	1.5
420	0.40	2.2	76.2	24.2	not determined	not determined	not determined
420	0.40	2.9	103.0	14.5	not determined	not determined	not determined
420	0.45	1.0	76.2	12.5	26.0	0.2	2.3
420	0.45	2.2	76.2	28.1	36.0	5.9	1.2
420	0.50	2.9	76.0	15.6	30.0	2.0	2.3
420	0.60	2.2	54.0	34.7	42.0	0.8	0.6
430	0.40	1.3	76.2	25.0	61.0	0.6	1.7
440*	0.25	2.0	54.0	28.5	37.0	5.7	not determined
440	0.27	2.0	54.0	29.1	not determined	not determined	not determined
440	0.40	3.3	54.0	42.7	not determined	not determined	not determined
440	0.54	3.2	54.0	43.0	not determined	not determined	not determined
460	0.60	3.2	32.0	24.5	not determined	not determined	not determined
$\beta$ -methylpyridine							
440	0.4	7.2	54.0	10.3	57.3	not determined	not determined
440	0.4	9.0	54.0	17.1	44.0	not determined	not determined
440	0.4	11.0	54.0	15.5	41.5	not determined	not determined

\*For  $\alpha$ -methylpyridine oxidation data see [1].

Table 3  
 Products Obtained by Oxidizing  $\alpha$ -,  $\beta$ - and  $\gamma$ -Methylpyridines over the Low Specific Surface Area Catalyst

Temperature, °C	Contact time, sec	Mole ratio		Pyridinaldehyde, calculated on		Pyridine-carboxylic acid, %	Pyridine, %
		O <sub>2</sub> : methyl-pyridine	Water : methyl-pyridine	Methylpyridine passed, %	Methylpyridine reacted, %		
$\gamma$ -Methylpyridine							
410	0.40	6.6	78.5	30.0	not determined	not determined	not determined
410	0.50	6.5	54.0	36.7	not determined	not determined	not determined
420	0.40	4.9	54.0	38.4	87.0	1.1	0.6
430	0.50	7.0	54.0	47.0	59.0	not determined	not determined
440	0.36	7.3	54.0	50.0	77.0	1.6	0.6
440	0.40	3.1	54.0	38.4	57.3	not determined	0.2
440	0.40	3.4	54.0	35.5	58.0	0.9	not determined
440	0.40	8.3	54.0	50.0	not determined	not determined	not determined
440	0.50	6.7	76.0	49.0	69.0	1.8	0.6
440	0.50	7.1	54.0	57.0	75.0	2.3	0.7
440	0.50	7.3	32.4	40.9	not determined	not determined	not determined
440	0.50	8.6	54.0	45.0	not determined	not determined	not determined
440	0.50	8.9	54.0	46.7	not determined	not determined	not determined
440	0.54	9.0	54.0	44.5	not determined	not determined	not determined
440	0.70	7.9	54.0	46.3	63.0	2.2	not determined
475	0.50	7.8	54.0	53.0	69.0	not determined	not determined
$\alpha$ -Methylpyridine							
440	0.3	1.0	54.0	2.2	91.0	not determined	not determined
440	0.54	9.1	54.0	22.0	55.5	not determined	not determined
440	0.76	7.0	54.0	33.0	57.0	not determined	not determined
440	0.80	5.0	54.0	39.1	77.0	not determined	not determined
440	0.90	6.0	54.0	40.0	82.0	not determined	not determined
440	0.96	4.6	54.0	45.0	91.0	not determined	not determined
$\beta$ -Methylpyridine							
420	0.55	7.0	54.0	11.6	50.4	0.5	—
435	0.66	14.0	54.0	22.1	70.9	3.9	—
440	0.40	1.00	54.0	1.7	11.3	—	—
440	0.40	3.2	54.0	5.3	29.6	—	—
440	0.40	18.0	54.0	14.7	58.8	0.7	—
440	0.40	22.6	54.0	13.9	47.9	5.8	—
440	0.40	28.6	54.0	16.0	66.6	not determined	—
440	0.50	20.0	54.0	21.0	55.0	not determined	—
440	0.60	22.0	54.0	26.0	61.9	1.4	—
450	0.40	20.0	54.0	19.5	65.0	2.5	—
460	0.40	25.0	15.6	21.6	56.8	0.8	—
480	0.40	20.0	54.0	23.0	76.5	1.3	—
480	0.40	20.0	75.0	13.8	54.5	not determined	—
480	0.40	21.0	38.0	15.8	48.0	3.5	—
480	0.40	41.0	54.0	18.2	41.0	not determined	—
480	0.40	48.0	54.0	13.3	39.2	not determined	—

36%, is obtained from  $\alpha$ -methylpyridine, while with  $\gamma$ -methylpyridine the total yield of pyridine is 3%, and with  $\beta$ -methylpyridine, only traces of pyridine are found in the oxidation products.

A different relationship is found for the yields of pyridinecarboxylic acids, the maximum values for  $\gamma$ ,  $\beta$ -, and  $\alpha$ -methylpyridines being respectively 10, 6, and 4%.

The different capacities of the isomeric pyridine-aldehydes to undergo further changes, which take place on the surfaces of the vanadium catalysts, can be explained largely by their different basicities.  $pK_a$  for  $\alpha$ -,  $\beta$ - and  $\gamma$ -pyridine aldehydes, as calculated from the pH [7] data, are 4.63, 4.40, and 4.99 i. e. the order of decreasing basicity is  $\gamma > \alpha > \beta$ . The abilities of these aldehydes to undergo further change varies in the same order. The value of the positive charge on the carbon atom of the aldehyde group, due to the effect of the nitrogen atom, determines the tendency of this carbon to react with the surface of the catalyst and with the chemisorbed molecules at the surface.

When the methylpyridines are oxidized over a vanadium oxide catalyst characterized by a low specific surface area ( $S_{sp} = 0.29 \text{ m}^2/\text{g}$ ), under optimum conditions the yields of the  $\alpha$ -,  $\beta$ -, and  $\gamma$  aldehyde isomers are respectively 45, 26, and 53%. With this particular catalyst, less total oxidation of the methylpyridines is found, its selectivity is very high, and the yields of all three isomeric aldehydes, calculated on the methylpyridine reacted, amount to 87% theory.

To obtain maximum yields of aldehydes over this catalyst, requires a larger quantity of air, securing twice the amount of oxygen compared with the working conditions obtained with the first catalyst.

This catalyst cuts the yields of the main by-products pyridine and pyridinecarboxylic acid.

As the composition of the reaction products stays the same as when using the first catalyst, it can be assumed that basically the same laws govern the way in which oxidation proceeds over either catalyst, but that only with diminished surface is the importance of the secondary conversion of the aldehydes on the catalyst surface cut.

## EXPERIMENTAL

**Starting materials.** Table 1 gives the properties of the starting materials. The apparatus and method of making the catalysts are described in previous papers [1, 3].

$\gamma$ -Methylpyridine was isolated from the  $\beta$ -picoline fraction of coal tar as its  $\text{COCl}_2$  complex, yield 10–15%.

The experiments were run at 390°–490° C, contact time 0.17–1.0 sec, and the dilution with air corresponded to an oxygen:methylpyridine mole ratio of 0.5 to 40.

In addition the reaction mixture was diluted with steam, in a mole ratio water:methylpyridine varying from 5 to 103.

**Analysis.** The purities of the starting methylpyridines, and the amounts of them unreacted, as well as the amounts of pyridine, were determined by GLC at 110°–150° C, carrier gas He, rate 1.3–1.5 l/hr. The liquid phases used were silicone elastomer E-301, and Apiezon M, supported on cellite 545 or on sodium chloride.

The amounts of unreacted methylpyridines were determined either by directly chromatographing a solution of the reaction product in water, or else the methylpyridines and pyridine were first extracted with ether. Internal standards were nonyl and octyl alcohols.

Pyridinaldehydes were determined gravimetrically (precipitated as oximes), by argentometric titration [1], or polarographically [4]. The pyridinecarboxylic acids were determined volumetrically, by titration with alkali, and identified by paper chromatography (solvent, *n*-BuOH saturated with water). In some cases the acids were determined polarographically. Tables 2 and 3 give results of runs.

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