BRIEF COMMUNICATIONS

THE VAPOR PHASE OXIDATION OF 3-PICOLINE ON TIN AND TITANIUM VANADATES*

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 6, pp. 1129–1133, 1969

UDC 547.821.41:824

The oxidation of 3-picoline with air on fused tin and titanium vanadates gives as the main reaction products nicotinaldehyde and nicotinic acid, the yield of which amounts to 45–50% of theory calculated on the alkylpipidine taken and 75–80% calculated on that which has reacted.

A considerable number of papers [2–7] have been devoted to the catalytic oxidation of 3-picoline (I). The majority of investigators have reported that over a wide range of conditions the main direction of the reaction is the destructive oxidation of (I) to oxides of carbon. Products of incomplete oxidation, nicotinaldehyde (II) and nicotinic acid (III) are usually formed with a yield not greater than 30–35%.

The aim of the present work was to study the vapor-phase oxidation of I on fused tin and titanium vanadate catalysts, which exhibit a high activity in the oxidative ammonolysis of alkylpyridines [8, 9]. The results of the experiments showed that when these catalysts are used the products of the oxidation of (I) contain (II), III, and oxides of carbon, and also pyridine (IV), nicotinonitrile (V), and hydrogen cyanide (VI). The yield of each of these compounds depends to a considerable extent on the conditions of performing the reaction.

Among the factors exerting a great influence on the process studied is the presence of steam in the reaction gases. One of us, with others, has previously established that in the vapor-phase oxidation of alkylbenzenes and pyridine derivatives the addition of steam favors the formation of aromatic and pyridinecarboxylic acids [10–12]. This is also shown by the results of other workers [4] who, by adding steam, succeeded in raising the yield of isonicotinic acid from 4-picoline considerably. Our experiments on the oxidation of I on titanium and tin vanadates have shown that when nonhumidified air is used the main reactions taking place are destructive ones. The addition of water to the initial reaction mixture permits the process to be directed to the predominant formation of II and III. The highest yield of oxygen-containing products with an unchanged carbon skeleton was found with the addition of from 50 to 70 moles of water per mole of 3-picoline.

The reaction temperature and the amount of air fed to the catalyst zone proved to have a no less substantial influence on the oxidation of I. As can be seen from the figure, the nature of the change in the yield of oxidation products as a function of the $I:O_2$ ratio is the same with both the catalysts studied: in the range of temperatures studied, with an increase in the feed of air the amount of II rises and the conversion of I and the yield of III pass through a maximum. On tin vanadate, the highest content of III in the catalysate is obtained in experiments at a temperature of 410–420° C, and on titanium vanadate at 345–360° C.

However, there are also fundamental differences in the catalytic action of tin and titanium vanadates. Thus, on thin vanadate the maximum yield of III under the optimum conditions is only 35%, and the total amount of II and III exceeds 45% of the theoretical value calculated on the I taken. Titanium vanadate shows a considerably higher selectivity for reactions of incomplete oxidation. Although on this catalyst II is obtained in somewhat smaller amounts, the yield of III reaches 50%. Since under these conditions about 30% of the I fed to the reactor passes through the catalyst unchanged, it must be considered that the selectivity of the main direction of the oxidative transformations of I connected with the formation of II and III is 75–77% in this case. Moreover, not more than 2–3% of the substance reacting is consumed in far-reaching oxidation reactions.

The presence of IV in the products of the oxidation of I is apparently the result of the destructive transformations of II and III and the intermediate labile compounds of the type $R{-}\dot{C}O$ and $R{-}CO{-}\dot{O}$ corresponding to them. Judging from the yield of IV, such reactions are less characteristic for titanium vanadate than for tin vanadate.

In the catalysates from high-temperature experiments carried out with a relatively long contact time, V is generally present. Its yield rarely exceeds 3–5%. The formation of nitriles of pyridinecarboxylic acids in the vapor-phase oxidation of pyridine derivatives have been observed by other workers: V was obtained in the oxidation of nicotine [13], and isonicotinonitrile has been observed in the product of the catalytic oxidation of a β-picoline fraction [14]. It must be assumed that the nitrile group of the cyanohydrins is formed in these cases by the reaction of intermediate products of the type of $R{-}\dot{C}O$, $R{-}CHO$, or $R{-}COOH$ with nitrogen-containing complexes formed on the surface of the catalyst from the nitrogen atoms of the decomposing pyridine rings.

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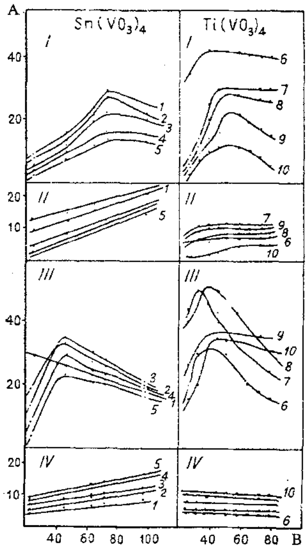
*Part LXIV of the series "Oxidation of organic compounds": for part LXIII, see [1].



Vapor-phase oxidation of I with air on tin and titanium vanadates: A) yield, %; B) oxygen in moles per mole of I. Rate of feed of I 68.1 g, and of water 928 g per liter of catalyst per hour; 1) 400° C; 2) 410° C; 3) 420° C; 4) 430° C; 5) 440° C; 6) 330° C; 7) 345° C; 8) 360° C; 9) 375° C; 10) 390° C; I) unchanged 3-picoline; II) nictoinaldehyde; III) nicotinic acid; IV) pyridine.