THE OXIDATION OF ORGANIC COMPOUNDS

XLIX. The Vapor Phase Catalytic Oxidation of Tris(hydroxymethyl)-4-picoline*

T. A. Afanas'eva, A. D. Kagarlitskii, and B. V. Suvorov

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In a study of the behavior of tris(hydroxymethyl)-4-picoline (I) under the conditions of vapor-phase oxidation on a vanadium-tin oxide catalyst, it was found that with the addition of 150–250 mole of water and 125–200 mole of O_2 per mole of I and a contact time of 0.35–0.45 sec, the main reaction product was isonicotinic acid (II), the yield of which amounted to 60–65% of theoretical, calculated on the I passed.

The catalytic vapor-phase oxidation of 4-alkylpyridines has been described in a number of papers [2–4].

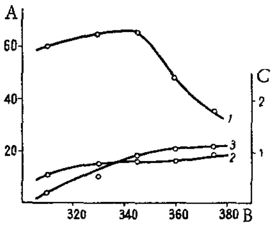

Fig. 1. Yield of the oxidation products of I as functions of the temperature: A) yield of II, %; B) reaction temperature, ° C; C) yield of CO and CO_2 in mole per mole of I; 1) II; 2) CO; 3) CO_2.

The available data indicates that one of the products of this reaction is isonicotinic acid (II). However, as a rule its yield is low. The main direction of the process is associated with the oxidative degradation of the six-membered ring and the formation of oxides of carbon. It appeared of interest to study the vapor-phase oxidation of the technically accessible [5] tris- (hydroxymethyl)-4-picoline (I), the behavior of which has not previously been studied under similar conditions.

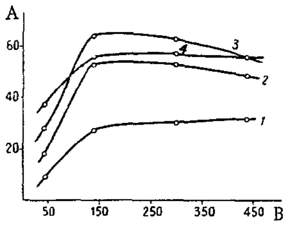

Fig. 2. Influence of steam on the oxidation of I to II: A) yield of II, %; B) steam in moles per mole of I; rate of feed of I, 80 g and of air, 9000 *l* per liter of catalyst per hour, time of contact 0.4 sec; 1) 360° C; 2) 375° C; 3) 390° C; 4) 405° C.

The experiments were carried out on an ordinary apparatus of the flow type with a granulated catalyst of fused tin vanadate. With a feed of 40 g (0.22 mole) of I, 560 g (31.1 mole) of water and 3000 *l* (28.1 mole of O_2) of air per liter of catalyst per hour, giving a contact time of 0.45 sec, the main reaction product was the acid II. As can be seen from Fig. 1, its yield varied with a rise in the temperature and reached a maximum at 345° C, 65% of the theoretically possible amount calculated on the I passed. Approximately the same dependence of the yield of II on the temperature has been observed with other ratios of the starting materials.

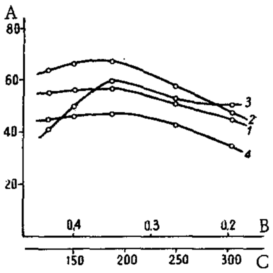

Fig. 3. Yield of II from the oxidation of I as a function of the time of contact and the amount of O_2: A) Yield of II, %; B) time of contact, sec; C) O_2 in mole per mole of I; rate of feed of I 40 g, of H_2O 560 g; 1) 330° C; 2) 345° C; 3) 360° C; 4) 375° C.

As in the oxidation of an alkylbenzene [6, 7], steam exerted a great influence on the course of the process. It can be seen from Fig. 2 that the maximum yield of II was obtained with a feed of 120–170 mole of water per mole of I. An increase in the concentration of water had almost no effect on the course of the reaction, but a decrease in the moisture content of the catalyst gases caused a marked fall in the yield of II and a rise in the proportion of far-reaching oxidative processes.

Figure 3 shows the results of experiments characterizing the yield of II as a function of the amount of air fed into the reactor and the time of contact. They demonstrate that the optimum amount of O_2 is 150–200 mole per mole of I and the optimum time of contact is 0.3–0.4 sec.

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*For part XLVIII, see [1].

EXPERIMENTAL

Compound I was obtained from a technical β-picoline fraction by the method of Koenigs and Happe [8]. Mp 156–157° C. Found, %: C 58.83; H 7.11; N 7.91. Calculated for $C_9H_{13}NO_3$, %: C 59.02; H 7.10; N 7.65%.

The experiments were carried out in a continuous apparatus with a quartz reaction tube 20 mm in diameter and 280 mm long containing a catalyst consisting of fused tin vanadate with a grain size of 3–5 mm. The I was fed into the reactor in the form of an aqueous solution by means of a bellows pump [9]. The reaction products were trapped by water in an absorber of the air lift type. The content of II in the absorption liquid was determined polarographically [10] on an oscillographic polarograph of type PO 5122 (the polarographic determination of II was performed by V. A. Serazetdinova). The background used was a 0.1 N solution of hydrochloric acid ($E_{1/2} = -0.86$ V with respect to the saturated calomel electrode). In individual experiments, for checking purposes, the II was isolated in the pure state. After crystallization from water with activated carbon, it did not melt below 315° C and had an equivalent of 123.1. Found, %: C 58.65; H 4.36; N 11.03%. Calculated for $C_6H_5NO_2$, %: C 58.54; H 4.09; N 11.38.

The content of CO and CO_2 in the catalyst gases was determined by gas chromatography.

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Institute of Chemical Sciences,
AS Kazakh SSR, Alma-Ata