

## AN INVESTIGATION OF THE VAPOR-PHASE CATALYTIC OXIDATION REACTION OF QUINOLINE

I. B. Chekmareva, E. S. Zhdanovich, and B. V. Suvorov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 5, pp. 842-844, 1968

UDC 547.831:542.943.7

The effect of water vapor, catalyst composition (tin vanadate), and quinoline air ratio in the contact gases on the yield of nicotinic and benzoic acids in the vapor-phase oxidation of quinoline has been investigated.

The catalytic vapor-phase oxidation of quinoline has not been sufficiently studied. The sole article available on the topic discusses the possibility of obtaining either nicotinic acid or pyridine by passing a mixture of quinoline vapors and air over a catalyst [1].

The present paper aims at a detailed study of the basic mechanism of this reaction. Preliminary experiments have shown that when quinoline is oxidized by air upon contact with suitable oxides, the reaction proceeds primarily with the combustion of the initial substance to oxides of carbon. Among the catalysts tried, tin vanadate ( $V_2O_5-SnO_2 = 1:1$ ) most favored the synthesis of incomplete combustion products, even in the alkylbenzene series [2, 3]. With this catalyst it was possible to obtain yields of up to 20% of the theoretical of nicotinic and of benzoic acids. Small quantities of benzaldehyde, 3-pyridine aldehyde, benzene, pyridine, maleic anhydride, and hydrocyanic acid were also obtained.

Generally, in the catalytic vapor-phase oxidation of organic compounds the introduction of water vapor into the reaction zone represses the combustion processes and increases the yield of incompletely oxidized products [3-5]. In this connection we studied the effect of water vapor on the catalytic oxidation of quinoline. An increase from 10-15 to 450 g of water per hour per liter of catalyst brought about a rise from 5 to 60-65% in the yield of nicotinic acid. The introduction of water vapor represses reactions leading to deep-seated oxidation, inasmuch as the quantity of oxides of carbon diminishes as the air moisture in the reaction zone increases. When participating in the reactions of vapor-phase oxidation water forms labile intermediate products consisting of hydrogen atoms and OH groups [6]. Evidently a

similar effect is observed in this case, since by passing a mixture of quinoline and water over tin vanadate in the absence of air, benzoic and nicotinic acids were obtained in the reaction products. The yield was 0.5-2.5%. Small quantities of benzene and pyridine were also obtained. In control experiments without water, however, oxygen-containing reaction products were absent. The yield of reaction products at various temperatures, under optimum conditions-54.0 g quinoline, 450 g water, 3950 g air (an 18-times excess) per liter of catalyst per hour during a 0.315 sec contact time-depended on the  $SnO_2$  content of the catalyst (Fig. 1).

It is evident from the data that, by increasing the  $SnO_2$  content of the catalyst, the yield of nicotinic acid increased and attained its maximum value (72.4%) with a  $V_2O_5-SnO_2$  catalyst composition of 1:1.5. A further increase in the  $SnO_2$  content did not increase the yield of either nicotinic or benzoic acid. It may be hypothesized that  $SnO_2$  in fused vanadium-tin catalysts increases the basicity of the catalyst and thus lowers its capacity of absorbing the pyridine nucleus.

Another factor exerting a substantial influence on the course of the reaction is the ratio of quinoline and air in the contact gases. Figure 2 shows the dependency of the yield of reaction products on the quantity of oxygen and the temperature, when employing  $V_2O_5-SnO_2$  catalysts with the compositions of 1:0.75 and 1:1.5. In both cases, an increase in the quantity of added oxygen (in the form of air) from 4 to 18 moles per mole of quinoline brought about a higher yield of nicotinic acid. When the second of the previously mentioned catalysts was employed at 420°, the yield of nicotinic acid attained 75%. The maximum yield of benzoic acid, 70.3%, was obtained by employing this same catalyst with a quinoline to oxygen ratio of 1:4, at 450°C. In addition, as the oxygen content of the reaction mixture increased, the quantity of unreacted quinoline diminished to 10-18%.

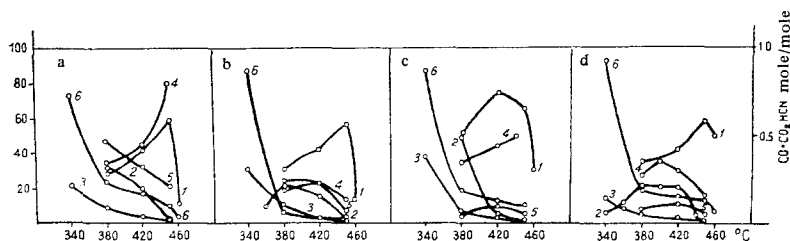


Fig. 1. Oxidation of quinoline on catalysts (K) consisting of  $V_2O_5$  with varying additions of  $SnO_2$ : a) K-1 ( $V_2O_5-SnO_2 = 1:0.75$ ); b) K-2 ( $V_2O_5-SnO_2 = 1:1$ ); c) K-3 ( $V_2O_5-SnO_2 = 1:1.5$ ); d) K-4 ( $V_2O_5-SnO_2 = 1:2$ ). 1) Nicotinic acid; 2) benzoic acid; 3) CO; 4)  $CO_2$ ; 5) HNC; 6) unreacted quinoline.

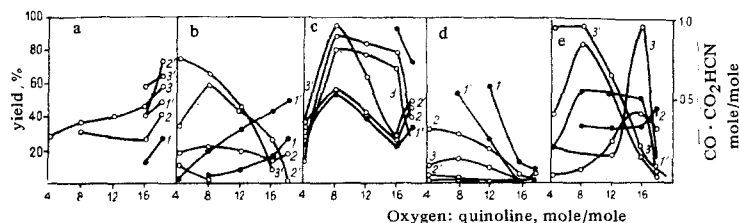


Fig. 2. Variation of yield with temperature and quantity of air: a) nicotinic acid; b) benzoic acid; c) CO<sub>2</sub>; d) CO; e) HCN, when employing catalyst K-1 and catalyst K-3, respectively; 1, 1') 380°; 2, 2') 420°, 3, 3') 450°. Curves 1, 2, 3 are for a catalyst of composition V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> = 1:0.75, Curves 1', 2', 3' are for a catalyst of composition V<sub>2</sub>O<sub>5</sub>-SnO<sub>5</sub> = 1:1.5.

To determine the effect of volume rate on the oxidation process, experiments were conducted with various quinoline additions, but with a constant molar ratio of the reactants, quinoline-air-water equal to 1:5.3:68.0. Varying the rate of quinoline addition with the limits 20–60 g per liter of catalyst per hour had no substantial effect on the yield of the main reaction products.

## EXPERIMENTAL

"Pure" quinoline, according to chromatographic analysis, contains isoquinoline as an impurity (Fig. 3). To eliminate this impurity, 26.0 g of phosphoric acid ( $d_4^{20}$  1.425) was added to 20 g of quinoline at 20°. The precipitated quinoline phosphate was filtered off, washed with 5.0 ml water, and air-dried for 24 hr. A product of 27.28 g of quinoline phosphate was obtained, mp 153–155°. A second precipitation was achieved by dissolving the substance in 17.5 ml of boiling water. After eliminating insoluble impurities, the filtrate was cooled to 5°, and allowed to stand 6 hr at this temperature. The precipitate was filtered off and air-dried for 24 hr. A yield of 17.25 g of quinoline phosphate was obtained, mp 160–161.7°. The crystals were decomposed with 10 ml of 40% NaOH. The organic layer was separated and dried for 10 hr over 27 g of KOH. The KOH precipitate was filtered off, and the filtrate distilled. The fraction boiling at 237.7–238.2° was collected;  $d_4^{20}$  1.0941;  $n_D^{20}$  1.6254;  $MR_D$  41.24 (calculated 41.28). The chromatographic analysis did not reveal any isoquinoline impurity (Fig. 3). Yield of the thus purified quinolines 9.5g (47.5%).

Fused catalysts were employed. A mixture of 182.0 g V<sub>2</sub>O<sub>5</sub> (1.0 mole) and 75.35 g of SnO<sub>2</sub> (0.5 mole) was heated at 1200–1300° for 2 hr, and the porridge-like mass was poured on an aluminum griddle. After cooling, the catalyst was pulverized, passed through a 3–5 mm-diameter sieve, and placed in the reaction chamber. The other catalysts were prepared in a similar way, except for a change in the ratio of the components.

The oxidation experiments were conducted in a stainless-steel, continuous flow-type installation, 1000 mm long and 21 mm in diameter. Automatic dispensers admitted the reactants into the reaction chamber.

The analyses were conducted according to the pattern of the experiment with a catalyst of V<sub>2</sub>O<sub>5</sub>-SnO<sub>2</sub> composition 1:1.5. Quinoline, water, and air were admitted at 420° into the reaction chamber at rates of 6.0 g, 50.0 g, and 474 liters per hr respectively. Contact time 0.38 sec, duration of the experiment, 2 hr. The reaction products were collected in water (100.0 ml) and cooled. The quinoline layer was separated from the aqueous; 1.60 g (13.3%) of unreacted quinoline was left over. The substances in the aqueous layer were extracted with chloroform (3 × 50 ml). The compounds in the chloroform extracts were dried over sodium sulfate and the solvent was distilled off, leaving behind 0.65 g (6.7% on the reacting quinoline) of benzoic acid, mp 120.5–122.0°,  $R_f$  0.43 (ascending; butanol, saturated with 1.5 N ammonia + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>). Found, %: C 68.81; H 4.88. Calculated for C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, %: C 68.85; H 4.93. The catalyst, now free of benzoic acid, was boiled with 3.0 g of activated carbon, the car-

bon was filtered off, and the filtrate was evaporated to dryness. Yield of 5.51 g of nicotinic acid (50.05% on the introduced or 72.5% on the reacted quinoline) was obtained, mp 233.5–235.7°;  $R_f$  0.20 (ascending isobutanol-ammonia, saturated with water 100:2; chromatography paper, Leningrad M-85). Found, %: C 58.50; H 4.00; N 22.80. Calculated for C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, %: C 58.53; H 4.07; N 22.76.

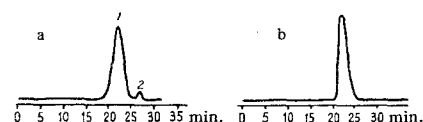


Fig. 3. Chromatogram of "pure" quinoline. a. 1) Quinoline, 2) isoquinoline; b. quinoline purified by phosphate. Chromatographic column was 2.4 m × 6 mm; stationary phase was polyethylene glycol adipate on diatomaceous brick (fraction 0.25–0.5 mm). Detector was microflame; carrier gas was hydrogen.

The determination of the gaseous reaction products was achieved by gas-liquid chromatography [7].

## REFERENCES

1. F. Komatsu and J. Ito, *Koru Taru*, 12, 493; 1960; Ref. Zhur. Khim., 14B514, 1961.
2. A. V. Solomin, B. V. Suvorov, and S. R. Rafikov, *Trudy, IKhN AN Kaz. SSR*, 2, 182, 1958.
3. B. V. Suvorov, S. R. Rafikov, and M. I. Khmura, *Izv. AN Kaz. SSR, ser. khim.*, no. 1 (15), 80, 1959.
4. B. V. Suvorov, S. R. Rafikov, and I. G. Anuchina, *Dokl. AN*, 88, 79, 1953.
5. A. S. Kostromin, V. S. Kudinova, S. R. Rafikov, B. V. Suvorov, and M. I. Khmura, *Izv. AN Kaz. SSR, ser. khim.*, no. 2 (14), 56, 1958.
6. V. S. Kudinova, S. R. Rafikov, K. D. Sagintaev, and B. V. Suvorov, *Zhur. Priklad. Khim.*, 35, 2313, 1962.
7. I. B. Chekmareva, V. I. Trubnikov, V. G. Berezkin, V. P. Pakhomov, E. S. Zhdanovich, and N. A. Preobrazhenskii, *Vestn. tekhn. i. ekonom. inform.*, no. 10, 26, 1964.

19 July 1966

All-Union Scientific-Research Institute of Vitamins, Moscow  
Institute of Chemical Sciences, AsKazakh SSR, Alma-Ata