

A STUDY OF THE OXIDATIVE AMMONOLYSIS OF QUINOLINE

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The oxidative ammonolysis of quinoline has been studied. The main products are pyridine, benzene, benzonitrile, and nicotinonitrile. Free nicotinic and benzoic acids and their amides are formed in small amounts. The gaseous products of the reaction are hydrogen cyanide and oxides of carbon. The most significant factors determining the direction of the process are the content of tin oxides in the catalysts, the concentration of ammonia in the feed gases, and the temperature of the reaction.

As is known [1-9], the oxidative ammonolysis of alkyipyridines is used in the synthesis of nitrils of pyridinecarboxylic acids. In this work, an attempt has been made to determine the possibility of applying the oxidative ammonolysis reaction to heterocyclic condensed systems, especially quinoline.

The experiments were carried out in a continuous apparatus with a fused mixed catalyst of oxides of vanadium with tin. It was found that the main products of the oxidative transformations of pure quinoline in the presence of ammonia and steam over a wide range of conditions are pyridine, benzene, benzonitrile, and nicotinonitrile. Free nicotinic and benzoic acids and their amides are formed in small amounts. Gaseous reaction products consist of hydrogen cyanide and oxides of carbon.

The simultaneous presence in the catalyzate of derivatives of benzene and of pyridine shows that the reaction takes place in two main directions, one of which begins with the cleavage of the heterocycle and the other with that of the aromatic ring of the initial compound. The relative weight of each of these directions depends on the conditions. The most significant in this respect were the influence of the amount of tin oxides in the catalyst, the concentration of ammonia in the feed gases, and the temperature. The results of several experiments characterizing the influence of the factors mentioned are given in Figs. 1 and 2. The experiments showed that vanadium catalysts consisting of fused vanadium pentoxide in the pure state or with small additions of tin dioxide possessed very slight selectivity from the point of view of the formation of carbonitriles and favored the formation of mainly combustion products. At the same time, on these catalysts the yield of aromatic compounds was, on the whole, higher than the yield of substances containing a heterocycle. With an increase in the content of tin dioxide in catalyst, the proportion of processes of incomplete oxidation rose. Simultaneously with this, the main direction of the oxidative ammonolysis of quinoline changed in the direction of the predominant formation of nicotinonitrile. As can be seen from Figs. 1 and 2, the largest amount of benzonitrile was obtained on a catalyst with the composition ($V_2O_5:SnO_2 = 1:0.75$), and the largest amount of nicotinonitrile on a catalyst with a ratio of vanadium pentoxide to tin dioxide of 1:1.5. The cause of the phenomenon considered must apparently be a change in the absorption properties of the catalyst with respect to the individual rings of the quinoline molecule: an increase in the amount of tin dioxide in the catalyst decreases its acidity and its capacity for absorbing the pyridine ring.

As follows from Fig. 1, the products of the incomplete oxidation of quinoline are formed with maximum yields with a ninefold excess of ammonia. At 450°C on the $V_2O_5:SnO_2 = 1:1.5$ catalyst the yield of

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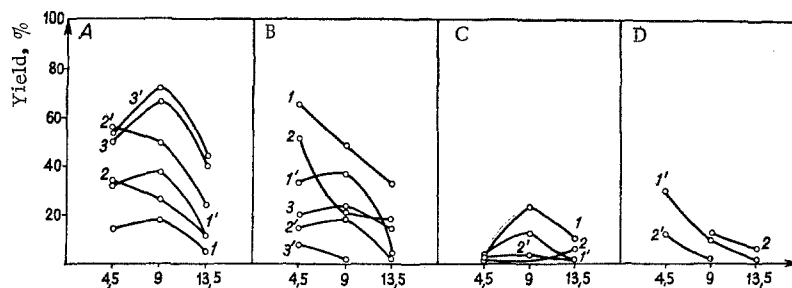


Fig. 1. Dependence of the yield of the products of oxidative ammonolysis on the amount of ammonia at: 1, 1') 380°C; 2, 2') 420°C; 3, 3') 450°C on, respectively, K-1 ($V_2O_5:SnO_2 = 1:0.75$) and K-2 ($V_2O_5:SnO_2 = 1:1.5$). A) Nicotinonitrile; B) benzonitrile; C) pyridine; D) benzene.

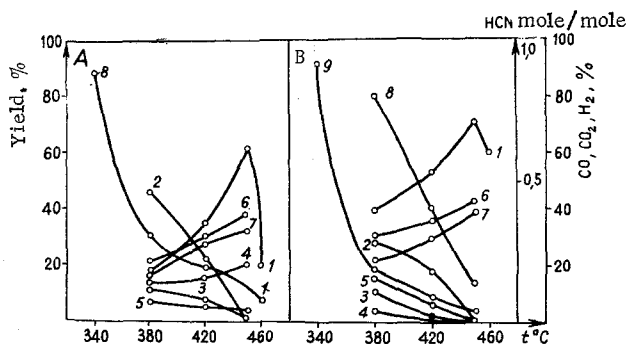


Fig. 2. Dependence of the field of products of the oxidative ammonolysis of quinoline on the temperature: A) NH_3 32.1 g, H_2O 182 g, $\tau = 0.171-0.202$ sec; B) NH_3 64.5 g, H_2O 365 g, $\tau = 0.161-0.191$ sec; 1) nicotinonitrile; 2) benzonitrile; 3) pyridine; 4) benzene; 5) CO; 6) CO_2 ; 7) H_2 ; 8) unchanged quinoline.

nicotinonitrile amounted to 72.1%. With a further increase in the feed of ammonia, the yield of monocyclic products fell. The greatest yield of benzonitrile was 66.5%, obtained at 380°C with a 4.5-fold excess of ammonia.

From the dependence of the yield of reaction products on the amount of ammonia, it may be assumed that the absorbed ammonia decreases the acidity of the catalyst and thereby the probability of the absorption of the pyridine ring.

It can be seen from Fig. 2 that with a rise in the temperature the yield of nicotinonitrile rises from 18-20 to 60-70% and simultaneously the yield of benzonitrile falls to zero. The yields of benzene and pyridine fall with a rise in the temperature.

A quantitative analysis of the gaseous products of the reaction showed that with a rise in the temperature the yields of carbon dioxide and hydrogen cyanide rise and the yield of carbon monoxide falls. The yield of gaseous products depends on the amount of ammonia and the temperature. As was to be expected, with a rise in the temperature the amount of products of far-reaching oxidation increases. However, the addition of ammonia suppresses combustion processes. Oxides of carbon are formed, as a rule, in the largest amounts in experiments with long contact times. This shows that, as in oxidation in the absence of ammonia, they are formed by the oxidative degradation of the carbon skeleton of quinoline.

Under the conditions of oxidative ammonolysis, the destruction of the aromatic ring of quinoline could be expected to lead to the formation of nitrogen-containing derivatives not only of nicotinic but also of picolinic and cinchomeronic acids. In actual fact, we detected only pyridine derivatives with substituents in the β position in the catalyzate. The reason for this must be connected with the instability of the corre-

sponding intermediate reaction products, apparently mainly carbonyl compounds and acids which, under the given conditions, lose side groups in the α position with respect to the heteroatom of the ring. Groups in the β position are relatively more stable, even in this case decarbonylation and decarboxylation processes do take place as is shown by the presence of small amounts of pyridine in the reaction products. Similar side reactions are accompanied by the formation of benzonitrile – benzene was found in the catalyzates from the overwhelming majority of the experiments.

Since experiments with pure quinoline have shown that it is converted into nicotinonitrile in high yield, it was interesting to determine the behavior of technical quinoline containing 27% of isoquinoline as impurity under similar conditions. With the passage of 5.4 g of quinoline, 3950 liters of air, 364.5 g of NH_3 , and 365 g of steam over a $\text{V}_2\text{O}_5:\text{SnO}_2 = 1:1.5$ catalyst at $\tau = 0.191$ sec, this material gave nicotinonitrile with a yield of 23.3 wt.%. Isonicotinonitrile was also found among the reaction products, its formation being the result of oxidative transformations of isoquinoline. Calculated on the isoquinoline fed the yield of isonicotinonitrile was 8.7% of that theoretically possible. The content of benzonitrile in the catalyzate did not exceed 1.5 wt.%.

Since the saponification of nicotinonitrile gives a good yield of nicotinic acid or its amide [10, 11], the results presented above permit the oxidative ammonolysis of quinoline to be recommended as a method for their preparation.

EXPERIMENTAL

I. A mixture of 12.0 g of quinoline (bp 237.7–238.2°C), 103.30 g of 15% ammonia, and 948.0 liters of air was passed through the catalyst ($\text{V}_2\text{O}_5:\text{SnO}_2 = 1:1.5$) at 450°C. The contact time was 0.177 sec. The trapping system was washed with 75.0 ml of water heated to 60°C, and the wash waters were combined and cooled to 20°C; 1.09 g (8.4%) of unchanged quinoline was separated. The nicotinonitrile was extracted with ether (4 × 50 ml), the extract was dried with calcium chloride and evaporated, and the residue was distilled. Yield 5.89 g (60.91%; 72.3% on the quinoline that had reacted). bp 240–241.5°C (690 mm). mp 48.5–50.0°C, λ_{max} 265 nm, $E_{1\text{cm}}^{1\%}$ 213.0. Found, %: C 69.18; H 3.80; N 25.99. $\text{C}_6\text{H}_4\text{N}_2$. Calculated, %: C 69.23; H 3.84; N 26.92.

II. At 420°C, 12.0 g of quinoline (bp 237.7–238.2°C), 103.30 g of 15% ammonia, and 948.0 liters of air were passed through the catalyst ($\text{V}_2\text{O}_5:\text{SnO}_2 = 1:1.5$) for 2 h. The amount of unchanged quinoline recovered was 1.23 g (10.3%). The reaction products were extracted with ether (5 × 50 ml), and the combined extracts were dried with calcium chloride and the ether was evaporated off. The residue was fractionated: first fraction – benzonitrile 1.55 g (16.0%), or 19.19% on the quinoline that had reacted. bp 191.5–198°C per 690 mm; d_4^{20} 1.0097; n_D^{20} 1.5306. Found, %: C 81.49; H 4.88; N 13.57. MR_D 30.77. $\text{C}_7\text{H}_5\text{N}$. Calculated, %: C 81.55; H 4.85; N 13.59. MR_D 30.75.

Second fraction – nicotinonitrile, 4.19 g (48.5% on the quinoline that had reacted). bp 240–242°C per 690 mm.

III. A mixture of 12.0 g of technical quinoline (67% of quinoline and 25% of isoquinoline, bp 237–239.0°C), 103.30 g of 15% ammonia, and 948.0 liters of air was passed through the catalyst ($\text{V}_2\text{O}_5:\text{SnO}_2 = 1:1.5$) at 450°C. The reaction products were trapped in 100.0 ml of water. The unchanged quinoline (1.44 g; 12.0%) was separated off, the products were extracted with ether (5 × 50 ml), and the extract was dried with calcium chloride and evaporated. The residue was distilled. First fraction – niconinonitrile. Yield 1.84 g (21.7%). bp 240.5–242.0°C/690 mm. mp 48–49.5°C. Mixed melting point 49–50°C. Second fraction – isonicotinonitrile. Yield 1.47 g (17.3%). bp 246–248°C/690 mm. mp 79–80.5°C, λ_{max} 278 nm, $E_{1\text{cm}}^{1\%}$ 215.0. A mixture of the isonicotinonitrile isolated (mp 79–80.5°C) and that obtained by the oxidative ammonolysis of γ picoline (mp 79.5–81.2°C) had mp 79.3–80.8°C. Found, %: C 69.18; H 3.81; N 26.89. $\text{C}_6\text{H}_4\text{N}_2$. Calculated, %: C 69.23; H 3.84; N 26.92.

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