

## OXIDATION OF ORGANIC COMPOUNDS

## LIV. The Oxidative Ammonolysis of the Trishydroxymethyl Derivative of 4-Picoline\*

T. A. Afanas'eva, A. D. Kagarlitskii, V. A. Serazetdinova, L. S. Saltybaeva, and B. V. Suvorov

*Khimiya Geterotsiklicheskikh Soedinenii*, Vol. 5, No. 4, pp. 672-674, 1969

UDC 547.821.411:542.943.7

It has been established that the main products of the oxidative ammonolysis of tris(hydroxymethyl)-4-picoline are isonicotinic acid and its amide and nitrile. At a molar ratio of the starting material to oxygen (in the form of air) to ammonia to water to 1:80-90:12-30:125-150 and with a contact time of 0.12-0.20 sec, these compounds can be obtained with yields of, respectively, 25-30, 5-10, and 45-50% of those theoretically possible on the basis of the raw material fed.

It is known that isonicotinic acid nitrile (I) is formed in the oxidative ammonolysis of 4-picoline [2-4]. In this work we have studied the oxidative ammonolysis of the tris(hydroxymethyl) derivative of 4-picoline (II) which, after the work of Koenigs and Happe [5] and of Hiller et al. [6], has become an available technical product.

The experiments were carried out on an apparatus of the flow type. Fused tin vanadate was used as the catalyst. As can be seen from Fig. 1, at 375-415° C with a feed of 106.5 g (0.58 mole) of II, 8000 liters (75 mole of O<sub>2</sub>) of air, 130.5 g (7.68 mole) of ammonia, and 1425 g (79 mole) of steam per liter of catalyst per hour and a contact time of 0.16 sec, the main reaction products are isonicotinic acid (III), its amide (IV), and I. Simultaneously, oxides of carbon and ammonium cyanide are obtained. The maximum yield of I, about 50% calculated on the II, was obtained at 405° C. Under these conditions the yields of III and IV were 18 and 10%, respectively. The catalyzates of low-temperature experiments contained a considerable amount of resinous substances of undetermined composition. In the high-temperature region, a large amount of oxides of carbon and ammonium cyanide was obtained.

The amount of air fed to the reaction zone and the time of contact of the reaction gases proved to have a substantial influence on the course of the process. The experimental results (Fig. 2) show that I, III, and IV can be obtained in the highest yield at a feed of 60-150 moles of oxygen (in the form of air) per mole of II with a contact time of 0.16-0.26 sec.

An important role in the oxidative ammonolysis of II is played by steam. It can be seen from Fig. 3 that an increase in the concentration of steam in the catalyst zone favors the formation of I and III to the greatest extent. At temperatures higher than 380° C, with an increase in the feed of steam from 50 to 150 moles per mole of II the yield of the products mentioned rose 1.5- to 2-fold, reaching 45% and 25%, respectively. It was possible to obtain the same results at a lower

temperature, but this was achieved at the expense of a further increase in the amount of steam in the initial reaction mixture.

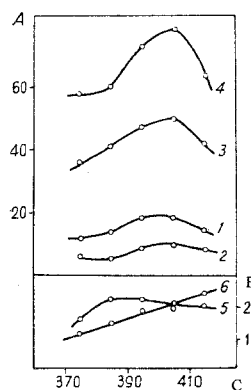


Fig. 1. Yield of the products of the oxidative ammonolysis of II as a function of the reaction temperature: A) yields of I, III, and IV, %; B) yields of CO<sub>2</sub> and NH<sub>4</sub>CN, moles per mole of II; C) reaction temperature, °C. 1) III; 2) IV; 3) I; 4) sum of I, II, and IV; 5) NH<sub>4</sub>CN; 6) CO<sub>2</sub>.

In the last two series of experiments described, 24-25 moles of ammonia was fed per mole of II. Taking the other reaction conditions into account, the optimum ratio of II to NH<sub>3</sub> was generally in the range 1:12-30. A decrease or an increase in the feed of ammonia outside these limits led to a substantial fall in the yield of all the products of incomplete oxidation, particularly I.

The results obtained show that the oxidative ammonolysis of II makes it possible to obtain I with a yield of up to 50%. Compounds III and IV are obtained simultaneously with a total yield of about 30%. Since I and IV are readily hydrolyzed by an aqueous solution of ammonia [7], the reaction described can be used for the synthesis of III.

## EXPERIMENTAL

The procedure for the purification of II and its physicochemical characteristics have been described previously [8], and so has the design of the apparatus for oxidative ammonolysis and the scrubber system for trapping the reaction products with a spray of water [9].

\*For part LIII, see [1].

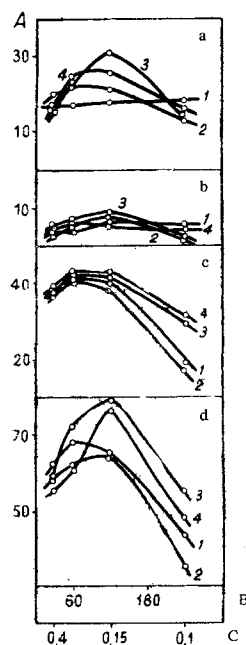


Fig. 1. Yield of the products of the oxidative ammonolysis of II as a function of the reaction temperature: A) yields of I, III, and IV, %; B) yields of  $\text{CO}_2$  and  $\text{NH}_4\text{CN}$ , moles per mole of II; C) reaction temperature,  $^{\circ}\text{C}$ . 1) III; 2) IV; 3) I; 4) sum of I, II, and IV; 5)  $\text{NH}_4\text{CN}$ ; 6)  $\text{CO}_2$ .

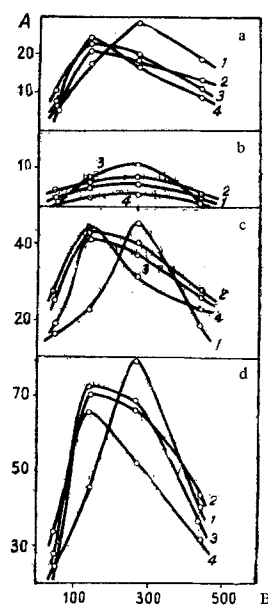


Fig. 2. Yield of the products of the oxidative ammonolysis of II as a function of the amount of air and the time of contact: A) yield, %; B) oxygen, mole per mole of II; C) time of contact, sec. Rate of feed of II 106.5 g, of ammonia 260 g, and of steam 1425 g/l of catalyst per hour; a) III, b) IV, c) I, d) sum of I, III, and IV; 1)  $375^{\circ}\text{C}$ ; 2)  $385^{\circ}\text{C}$ ; 3)  $405^{\circ}\text{C}$ ; 4)  $415^{\circ}\text{C}$ .

The products of the oxidative ammonolysis of II were analyzed polarographically. All the determinations were carried out on a type PO-5122 oscillographic polarograph. The cell was thermostatted at  $25 \pm 0.2^\circ \text{C}$ . The dropping electrode at  $h = 22.5 \text{ cm}$  and on open circuit had the characteristics  $m = 2.4 \text{ mg/sec}$ ,  $t = 5.5 \text{ sec}$ ,  $m^{2/3}t^{1/6} = 2.04 \text{ mg}^{2/3} \text{ sec}^{1/6}$ . The comparison electrode was an external saturated calomel half-cell. In the determination of I, the oxygen was eliminated from the solution by purging the cell with pure argon.

For the determination of I, 10 ml of the reaction liquid was extracted with benzene ( $5 \times 2 \text{ ml}$ ). The resulting extract was diluted with benzene to 15 ml. A sample with a volume of 2–3 ml was placed in a 25-ml measuring flask, 21 ml of a 0.1 N ethanolic solution of hydrochloric acid was added, and the solution was made up to the mark with ethanol. The concentration of I was calculated from the measured strength of the limiting current ( $I_a$ ) with  $E_{\text{peak}} = -0.806 \text{ V}$ , using a calibration graph.

After the I had been eliminated, III and IV were determined in the reaction liquid. To determine III a sample with a volume of 2–5 ml was diluted with 0.1 N lithium hydroxide to 25 ml. The concentration of III was determined from the strength of the limiting current with  $E_{\text{peak}} = -1.92 \text{ V}$ . Another sample (2–5 ml) was treated with 2 ml of Izmailov and Pivneva's veronal buffer solution with  $\text{pH} = 12$ , and the total volume of the sample was brought to 25 l with water. The concentration of the IV was calculated from the strength of the limiting current with  $E_{\text{peak}} = -1.52 \text{ V}$ .

The presence of ammonia and II did not interfere with the determination of the products mentioned above.

In a number of experiments, the reaction products were isolated in the pure state and characterized. The method of identification has been given previously [4].

## REFERENCES

1. B. V. Suvorov, N. R. Bukeikhanov, and V. S. Kudinova, *Izv. AN KazSSR, ser. khim.*, **2**, 86, 1967.
2. F. Porter, M. Ershak, and I. N. Cosby, U.S. patent no. 2510605; *C. A.*, **45**, 187, 1951.
3. G. Mayurnik, A. F. Moschetto, H. S. Bloch, and J. V. Scudi, *Ind. Eng. Chem.*, **44**, 1630, 1952.
4. B. V. Suvorov, S. R. Rafikov, V. S. Kudinova, and B. A. Zhubanov, *ZhPKh*, **32**, 1642, 1959.
5. W. Koenigs and G. Happe, *Ber.*, **36**, 2904, 1903.
6. M. Yu. Lidak, S. A. Hiller, and N. N. Naumenko, *Izv. AN LatvSSR, ser. khim.*, **12**, 83, 1953.
7. I. A. Arkhipova, B. V. Suvorov, and S. R. Rafikov, *ZhPKh*, **35**, 389, 1962.
8. T. A. Afanas'eva, A. D. Kagarlitskii, and B. V. Suvorov, *KhGS [Chemistry of Heterocyclic Compounds]*, **142**, 1968.
9. A. D. Kagarlitskii, V. S. Kudinova, S. R. Rafikov, D. Kh. Sembaev, and B. V. Suvorov, *Izv. AN KazSSR, ser. khim.*, **2**, 23, 1966.

15 February 1967

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