# TRANSFORMATION OF ALKALOID ANABASIN
INTO NICOTINONITRILE

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The possibility of preparing nicotinonitrile from the natural alkaloid anabasin via oxidative ammonolysis using a vanadium—titanium catalyst ($V_2O_5:TiO_2$ = 1.0:0.5) is examined.

Anabasin, which occurs in natural underbrush and cultured plantations of *Anabasis aphilla*, is oxidized by nitric acid or potassium permanganate to nicotinic acid (provitamin PP) [1]. It seemed interesting to subject this alkaloid to oxidative ammonolysis [2], which would enable pyridine derivatives with alkyl substituents in the 3-position of the ring to be converted with good yield into nicotinonitrile [3]:
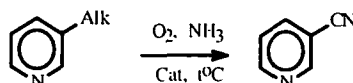

Then nicotinonitrile could be quantitatively hydrolyzed to the free acid or the amide (vitamin PP) [4]:
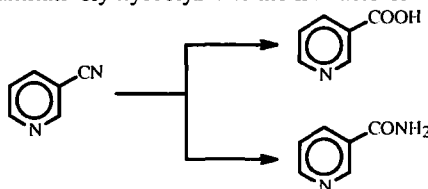
Oxidative ammonolysis of anabasin was studied on a fused oxide V—Ti catalyst ($V_2O_5:TiO_2$ = 1.0:0.5) at varying temperature (360-440°C) and varying amounts of NH_3 (8-25 moles) and H_2O (60-155 moles) per mole of anabasin.

The principal product was nicotinonitrile. Unreacted alkaloid, picolinonitrile, pyridine, and ammonium cyanide were found in small quantities in the catalysates. The off gases contained mainly CO_2 and N_2. The overall process can be written:
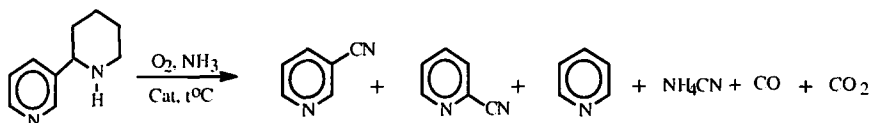
The transformation of anabasin can proceed in three possible directions. The first form nicotinonitrile is predominant. It involves oxidative decomposition of the piperidine ring. The α-C atom that is bound to the pyridine ring is retained and converted to a cyano group. Analogous conversions are observed through decomposition of the pyridine ring. These form 2-cyanopiperidine, which is dehydrated under the reaction conditions to picolinonitrile. Finally, the bond between the rings can cleave to give pyridine and piperidine, which is dehydrated into pyridine. The results that illustrate the effect of the basic parameters of the studied process on its route are given below.

The extent of conversion of the starting alkaloid smoothly increases with increasing reaction temperature and contact time. The product yield also increases, reaching a maximum at 420°C and 0.76 s contact time (Figs. 1a and -b). Increasing these parameters further increases the amount of destructive reactions.
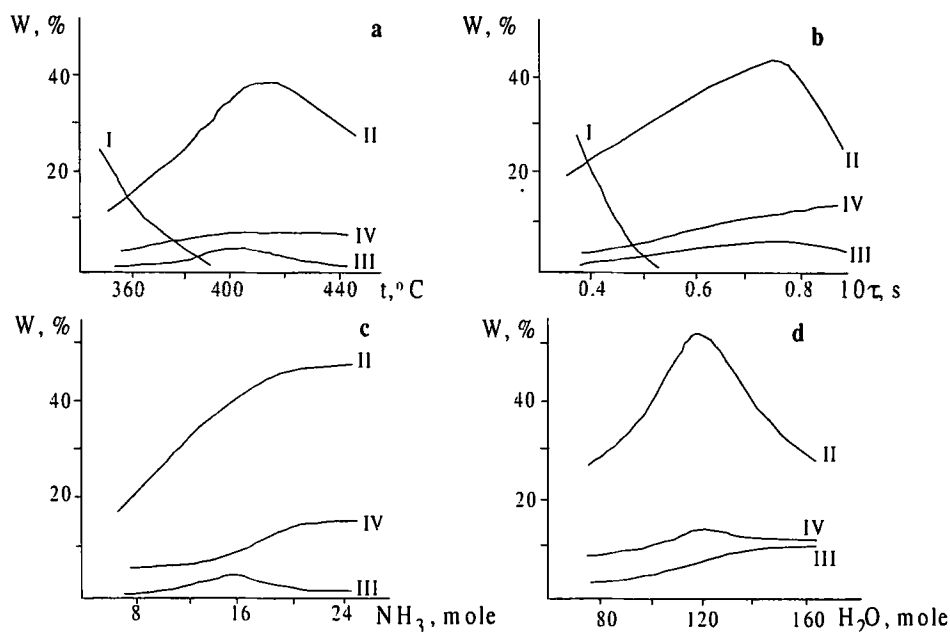
Fig. 1. Yield from oxidative ammonolysis of anabasin as a function of temperature (a), contact time (b), ammonia concentration (c), and amount of water (d): $t = 420°C, \tau = 0.76$ s; anabasin:NH_3:H_2O = 1:10:70 (a, b), 1:(8-25):100 (c), 1:12:(60-155) mole/mole (d); anabasin (I), 3-CNPy (II), 2-CNPy (III), Py (IV).

The concentrations of NH_3 and H_2O vapor in the contact zone substantially affect the process. It was found that the yield of nicotinonitrile reaches a maximum for 20-25 moles of NH_3 and 120 moles of H_2O per mole of anabasin (Figs. 1c and -d). Water in large quantities begins to compete with anabasin for surface sites. This decreases the selectivity for nicotinonitrile formation [5].

Thus, the results demonstrate that oxidative ammonolysis can be used to transform the available alkaloid anabasin into nicotinonitrile, which forms in 46-52% yield (based on starting material) on the studied catalyst.

EXPERIMENTAL

Experiments were performed in a continuous reactor [5] with a stainless-steel (1Kh18N10T) tube (20 × 500 mm). The anabasin:aqueous ammonia mixture was fed into the reactor by a MC-706 pump. The air flow rate was monitored with a rheometer. The reaction products were trapped in an Erlift water scrubber.

The starting material was anabasin free-base obtained from the hydrochloride. Pure anabasin is a colorless liquid with bp 280.9°C and $d_4^{20} = 1.0481$.

The catalyst was prepared by the literature method [6]. Products were analyzed by GLC (Khrom-5 instrument) with a flame-ionization detector. The stationary phase was SE-30 on Chromaton N-AW-HMDS in a glass column (2.5 m × 3.0 mm). The following conditions were used: vaporizer temperature 190°C, column temp. 160°C, detector temp. 200°C. The carrier gas flow rate was 30 ml/min; air, 300 ml/min; H_2, 30 ml/min.

In addition to chromatographic analysis, pyridine, nicotinonitrile, and picolinonitrile were in some experiments extracted from the scrubber liquid by CH_2Cl_2 and fractionated. The boiling and melting points of the nitriles corresponded to the literature values: nicotinonitrile, mp 48°C, bp 240°C; picolinonitrile, mp 26°C, bp 118°C. These were also identified by elemental analysis.

REFERENCES

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