CATALYTIC TRANSFORMATIONS OF DIETHYLAMINE 
OVER PLATINUM AND PALLADIUM CATALYSTS

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We have shown [1] that in presence of platinized charcoal at 310° diethylamine undergoes dehydrocyclization with formation of the five-membered heterocyclic system of pyrrolidine. Under the conditions of the reaction this system is unstable and undergoes further transformations. The first stage of this reaction— the formation of pyrrolidine—is probably analogous to the C₆-dehydrocyclization of hydrocarbons [2], which goes under the same conditions. In presence of a number of metal and oxide catalysts, aliphatic amines fairly readily undergo change. They are dehydrogenated to nitriles, deaminated with formation of olefins and low amines (or ammonia), and undergo various disproportionation reactions [3]. Recently, a number of patents have been devoted to these transformations [4].

In the case of aliphatic-aromatic amines, apart from the reactions enumerated above, the formation of the indole system has been reported [5]. In the case of aromatic amines, the formation of carbazole has been observed [6]. However, it appears that we observed the cyclization of aliphatic amines into pyrrolidines for the first time. The extension of our knowledge of this new reaction of aliphatic amines is therefore of decided interest.

In the present work we studied the behavior of diethylamine over platinized charcoal over a wider temperature range (200-310°) and showed that the yields of the main reaction products then vary.

Also, to determine how far the analogy of this reaction to the C₆-dehydrocyclization of hydrocarbons extends, we also conducted a series of experiments with palladized charcoal. It is known that platinized charcoal is an extremely specific catalyst for the C₆-dehydrogenation of hydrocarbons. The other group VIII metals investigated in this reaction (Ni, Pd, Rh, Ir, Os) are inactive, at least in absence of a carrier gas [7]. It was found, however, that in the cyclization of amines palladized charcoal also has fairly high activity.

The course of the reaction is complex over both catalysts. Thus, analysis by gas-liquid chromatography showed that even the liquid catalyzates obtained over platinum at 240°, but particularly those obtained in the range 260-300°, consist of at least 7-9 substances. It might be supposed that we are dealing with the simultaneous occurrence of a whole series of parallel and consecutive reactions. However, there are grounds for the view that the reactions are grouped around two main courses of reaction. In the first place, the destructive cleavage of the original molecule occurs with formation, probably, of ethylene and ethylamine. Ethylamine is further dehydrogenated to acetonitrile, and ethylene is hydrogenated to ethane. In the second place, diethylamine is cyclized to pyrrolidine, the hydrogenolysis of which gives butylamine and, further, butyronitrile. Part of the pyrrolidine is dehydrogenated to pyrrole. This is illustrated by the scheme given below:

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\begin{align*}
\text{CH}_2\text{CH}_2\text{NH}_2 + \text{CH}_3\text{CH} = \text{CH}_2 \rightarrow \text{CH}_3\text{CN} + \text{C}_2\text{H}_6 \\
\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3 + \text{CH}_3\text{CH} = \text{CH}_2 \rightarrow \text{CH}_3\text{CN} + \text{C}_2\text{H}_6
\end{align*}
\]
Fig. 1. Increase in the acetonitrile content of diethylamine catalyzates obtained over platinized (1) and palladized (2) charcoals with rise in temperature.

Fig. 2. Increase with rise in temperature of the butyronitrile content of diethylamine catalyzates formed over platinized (1) and palladized (2) charcoals.

This scheme is confirmed by the fact that acetonitrile and butyronitrile were isolated by us in the pure state from catalyzates obtained over platinized charcoal; pyrrole was identified in them by means of gas chromatography. We have detected butylamine in analogous catalyzates earlier [1]. At the same time we proved the presence of ethane and hydrogen in the gaseous reaction products. We did not succeed in proving the presence of pyrrolidine in the catalyzates. We must point out particularly that under the conditions of our experiments the possibility of the formation of butyronitrile from acetonitrile, for example via CH₃C(=NH)CH₂CN, was excluded. By special experiments it was proved that acetonitrile remains almost unchanged in contact with platinized charcoal at 280°. In the experiments with platinized charcoal the acetonitrile content of the catalyzate rises rapidly with rise in temperature, particularly from 240° upward. The same type of behavior is observed also for butyronitrile. The increase in the contents of the two nitriles in the catalyzates is shown in Figs. 1 and 2. Unchanged diethylamine predominates in catalyzates obtained at 200-220° and is almost absent in catalyzates obtained at 270-310°.

To isolate the diethylamine transformation products in the pure state catalyzates obtained in a special series of experiments over platinized charcoal at 260-300° were combined and fractionated through a column of about 20-plate efficiency. In the course of the fractionation, the results of which are presented in Fig. 3, two fairly large plateaux were observed, corresponding to acetonitrile (fractions V-VII) and butyronitrile (fractions IX and X). Judging by their constants, the two nitriles were isolated in the pure state. Also, from butyronitrile we prepared crystalline p-butyrotoluidide, which melted without depression when mixed with a known sample. Further identification of the two nitriles was effected by gas-liquid chromatography. Also, by means of gas-liquid chromatography, pyrrole was identified in fraction XI.

An analogous series of experiments with diethylamine was carried out in presence of palladized charcoal. The composition of the catalyzates was qualitatively the same as over platinized charcoal. However, with rise in temperature the content of unchanged diethylamine in the catalyzates diminished considerably more slowly than in the case of platinized charcoal. The increase in the content of butyronitrile, and particularly of acetonitrile, with rise in temperature goes more slowly and smoothly over palladized charcoal than over the platinized