

CATALYTIC DEHYDROCYCLIZATION OF DIETHYL ETHER
FORMING A FIVE-MEMBERED HETEROCYCLIC SYSTEM

(UDC 542.97)

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Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 7,

pp. 1352-1354, July, 1964

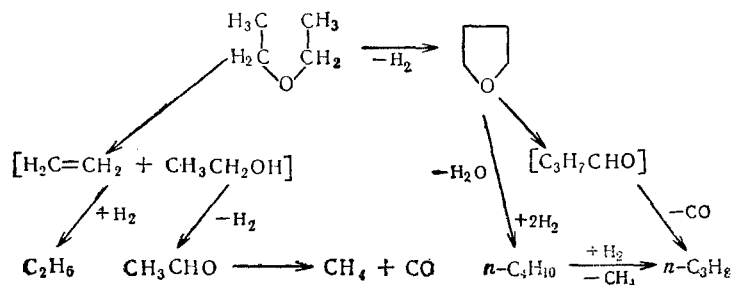
Original article submitted December 29, 1963

We have recently established that not only hydrocarbons, [1] but also compounds including a heteroatom, in particular, diethylamine [2] can be successfully subjected to catalytic dehydrocyclization, forming a five-membered ring. It was found that in the presence of platinized and palladium-treated charcoal at temperatures of 200-300°, it undergoes complex transformations. Among them, there are two main reaction directions: 1) destructive decomposition of the initial amine at the relatively weak C-N bond, forming ethylamine and then acetonitrile; 2) cyclization of diethylamine to pyrrolidine, with further conversion of the latter to a pyrrole.

It was of undoubted interest to attempt to extend this reaction to compounds with two heteroatoms, in particular, to simple ethers. For this purpose, diethyl ether was passed over certain noble metals of group VIII, deposited on charcoal: Pt/C, Pd/C, Ir/C, Os/C and Rh/C, at 250-300°. By analogy with the hydrocarbons, and especially with the amines, we might expect the appearance of new C-C bond, forming tetrahydrofuran and products of its further transformation. And in fact, the results that we obtained show that a whole series of complex processes proceed to one degree or another on the surface of all the catalysts enumerated above. Moreover, apparently the primary event of cyclization of the ether, forming tetrahydrofuran, is common to all five catalysts. Tetrahydrofuran and butane were identified in the catalyzates of the ether, passed over Pd/C, Rh/C and Ir/C, by the method of gas-liquid chromatography. Fig. 1 gives a chromatogram of the catalyzate of ether passed over Ir/C (250°), while Fig. 2 gives a chromatogram of the same catalyzate with a small addition of known tetrahydrofuran. It can easily be seen that peak 2 in the second case is substantially enlarged, while the dimensions of the remaining peaks remain the same.

The catalyzates obtained by passing ether over Pt/C and Os/C did not contain THF. However, butane and propane were identified in them. The latter may be obtained both as a result of decomposition of the THF itself [3], and by cracking of butane (on Os/C). The increased tendency toward hydrolysis, manifested in the case of Pt/C and Os/C, is apparently a specific feature of these catalysts, which we also noted earlier, both for the example of hydrocarbons on Os/C [4], and that of amines on Pt/C [2]. In the catalyzate obtained by passing ether over Rh/C, in addition to the products enumerated above, we identified acetaldehyde, apparently formed as a result of hydrogenolysis of the ether at the C-O bond, followed by partial dehydrogenation. The scheme of acetaldehyde formation is analogous to the scheme of formation of acetonitrile in the case of the transformations of diethylamine.

As a result of the above, the basic transformations of diethyl ether, proceeding on the surface of the noble metals of group VIII, can be depicted by the following scheme



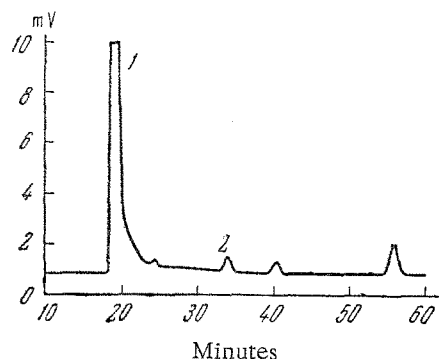


Fig. 1. Chromatogram of the catalyzate of diethyl ether, passed over Ir/C at 250° 1) diethyl ether; 2) tetrahydrofuran.

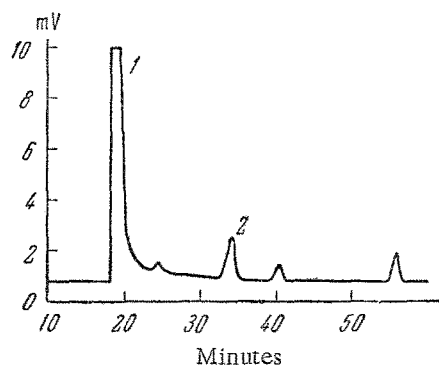


Fig. 2. Chromatogram of the catalyzate of diethyl ether, passed over Ir/C with an addition of tetrahydrofuran. 1) diethyl ether; 2) tetrahydrofuran.

of the metal lattice. Of course, our new data [4], pertaining to the hydrogenolysis of hydrocarbons in the presence of the same catalysts, lead to the idea that this mechanism of hydrogenolysis is compulsory only for a platinum catalyst. Apparently on certain other noble metals of group VIII, a doublet scheme of hydrogenolysis and dehydrocyclization is also possible. The mechanism of the dehydrocyclization of ether will be considered in the near future.

EXPERIMENTAL

The catalysts (Pt/C, Pd/C, Ir/C, Os/C and Rh/C) were prepared according to the method of Zelinskii and Turova-Polyak [6] by reduction of the corresponding salts with formalin, and contained 20% by weight of metal. The ether [b.p. 34.6° (760 mm); n_D^{20} 1.3527] preliminarily distilled on a column with an efficiency of 20 theoretical plates, was passed over the catalysts at 250 and 300° without a carrier gas, at a space velocity of $\sim 0.4 \text{ h}^{-1}$. The yield of the liquid catalyzates was 50-70% of the weight of the ether passed through; they possessed n_D^{20} from 1.3520 to 1.3538 and contained up to 3% THF. The analysis was performed on a capillary chromatograph, equipped with a microflame ionization detector and a copper capillary 50 m long. The liquid phase was squalane.

CONCLUSIONS

When diethyl ether is placed in contact with certain noble metals of group VIII, dehydrocyclization of the ether occurs, forming tetrahydrofuran and its decomposition products. The observed reaction is analogous to C_5 -dehydrocyclization of hydrocarbons and cyclization of secondary amines to pyrrolidine.

This scheme is confirmed by the fact that THF, acetaldehyde, butane, and propane were identified by the method of gas-liquid chromatography in catalyzates obtained. The gaseous reaction products contain hydrogen, methane, ethane, propane, butane, and carbon monoxide, in one ratio or another, depending on the nature of the catalyst and the temperature of the experiment. We should mention that the gaseous products obtained in the passage of diethyl ether over Pt/C contained 29.2% by volume CO, 30.2% CH_4 , and 25.0% C_2H_6 , which is in good agreement with the scheme cited, not only qualitatively, but also quantitatively.

Noteworthy is the fact that a number of not yet identified substances, the amounts of which are commensurate with the amount of THF, were chromatographically detected in the liquid portion of the catalyzate, in addition to the initial ether, tetrahydrofuran (on Pd/C, Rh/C, and Ir/C), and acetaldehyde (on Rh/C). These peaks may correspond to condensation products of butyraldehyde, which, according to the data of Shuikin and Bel'skii [3], is formed from THF under these conditions. Thus, the material obtained shows that in the presence of the noble metals of group VIII at 250-300°, diethyl ether undergoes dehydrocyclization, forming THF. This fact, in conjunction with the data on the transformations of hydrocarbons [1] and amines [2], permits us to conclude that the reaction of dehydrocyclization with formation of five-membered ring is apparently a sufficiently general reaction.

The new data on the transformation of diethyl ether to THF and partial decomposition of the latter, forming butane, are in good agreement with the concepts of the mechanism of C_5 -dehydrocyclization of hydrocarbons. According to these representations [5], the reaction mentioned proceeds with formation of a transition complex, absorbed flat on the surface of the catalyst in such a way that the atoms of the reacting substance are arranged in definite interstices

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