DEHYDRATION OF ALCOHOLS TO ETHERS IN THE PRESENCE OF METAL CATALYSTS

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The transformation of *n*-propanol and *n*-butanol in the presence of hydrogen, on platinum, palladium and copper catalysts have been studied, using the impulse (microreactor) technique, in the temperature range between 150 and 350 °C. Beside the process of dehydrogenation resulting in the formation of aldehydes (10—20%), also an intermolecular dehydration could be observed, in the course of which dipropyl ether and dibutyl ether (10—30%) have been formed on each of the three catalysts. These experimental observations represent suitable data for the investigations on the nature and mechanism of the effect of metal catalysts.

Metal catalysts are considered to be substances catalysing chiefly the hydrogenation and dehydrogenation, both theoretically and industrially. Also the theory of metal catalysis has been formed and developed from this point of view. It was only PINES and STEINGASZNER [1] who reported on their experiments on intermolecular dehydration, according to which the conversion of alcohols to ether is catalysed by nickel.

Studying the transformation of different carbon compounds on metal catalysts, by means of impulse (micro reactor) technique, it has been observed that over platinum and palladium catalysts on thermolit carrier, as well as on Raney-type copper catalyst, in the presence of hydrogen not only the expected aldehydes but, owing to the intermolecular dehydration process, also ethers formed from propanol and butanol. (For some of the experimental data see Table I.)

*Table I**

Catalyst	Starting material	Temperature °C	Composition of the product formed (%)		
			Aldehyde	Dialkyl ether	Alcohol
Pt/T	*n*-butanol	250	10—15	20—25	55—60
Pt/T	*n*-propanol	300	20—25	15—20	35—40
Pd/T	crotyl alcohol	150	15—20	35—40	40—45
Cu/Al	*n*-butanol	350	30—35	10—15	30—35

* T = thermolit carrier. Concerning the experimental method applied, as well as the preparation of catalysts see our earlier paper [2]. The microreactor was made quartz.

For the explanation of ether formation, the following observations were found relevant:

1. The ether formation is not catalysed by the carrier.
2. Using helium as carrier gas, no ethers were formed on Pt/T catalyst.
3. Pt/T catalyst previously treated with ammonia proved to be inactive from the point of view of ether formation.
4. After heat treatment and desorption of ammonia, the catalyst described in point 3 proved to be active again.
5. On Pt/T catalyst, in the presence of hydrogen, significantly more dibutyl ether was formed from the mixture of *n*-butanol and butyraldehyde, than from *n*-butanol alone.

On the basis of the experiments described above, it can be stated that the surface sites with specific activity of the metal catalysts are responsible for the ether formation. The hydrogen has a double role; on the one hand, it plays a part in the formation of the active sites, and on the other hand, it makes possible the ether formation by the following mechanism:

$$CH_3—CH_2—CH_2—CHO + C_4H_9—OH \rightarrow C_3H_7—\underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}—O—C_4H_9 \xrightarrow{H_2}$$

$$\rightarrow C_4H_9—O—C_4H_9 + H_2O.$$

Of course, a lot of important questions arise in connection with this problem, the solution of which, as well as the clearing up of the mechanism of the effect of the metal catalysts used require further more, detailed investigations.

References

[1] *Pines, H., P. Steingaszner:* J. of Catalysis **10,** 60 (1968).
[2] *Bartók, M., S. Fényi:* Acta Phys. et Chem. Szeged **12,** 157 (1958).

ДЕГИДРАТАЦИЯ СПИРТОВ В ЭФИРЫ НА МЕТАЛЛИЧЕСКИХ КАТАЛИЗАТОРАХ

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Нами было изучено превращение пропилового и бутилового спиртов в импульсном режиме на катализаторах платины, палладия и меди в присутствии водорода при температурах 150—350°. Главными направлениями являются образования соответствующих альдегидов и простых эфиров.