

## INVESTIGATIONS IN THE FIELD OF DIOLS AND CYCLIC ETHERS. XXVIII<sup>1</sup>

### Study of Vapour—Phase Transformation of Propanediol—1,3 on Raney—Type Catalysts

M. BARTÓK and L. ZALOTAI

Institute of Organic Chemistry, Attila József University, Szeged

(Received December 1, 1967)

The vapour-phase transformation of propanediol-1,3 in the presence of Raney-type catalysts such as Cu—Al, Pd—Al, Co—Al, Ni—Al, Zn—Al and Cu—Zn—Al was investigated in the temperature range of 170—300 °C. Directions of the different reactions were measured as the function of temperature, rate of feed and type of catalyst applied.

Main processes are considered to involve intramolecular dehydration producing propionaldehyde and allyl alcohol, fragmentation producing ethylene. Primary processes are followed by secondary transformations depending on the catalysts. Cu—Al catalysts are more effective in the reaction of propanediol—1,3  $\rightarrow$  propionaldehyde + H<sub>2</sub>O than transition metals. A maximum yield of 76% can be obtained in the presence of a Cu—Al catalyst between 200 and 250 °C.

The investigations of the authors carried out with 1,3-diols in the presence of various contacts form a part of the chemistry of 1,3-bifunction systems. The object of these experiments was to find regularities suitable to express the dependence of the transformation of 1,3-diols in various directions on their structure and on the different conditions of the reaction. As a method for studying the chemistry of 1,3-diols the rather "neglected" field of contact catalysis in the vapour-phase was chosen and as catalyst the "skeleton catalyst" of Raney-type, a previously never applied type, was selected. In the present paper account is given on the experiments carried out with trimethyleneglycol, an 1,3-diol of the simplest structure.

Transformation of propanediol-1,3 was studied in a flow system at temperatures ranging from 170 to 300 °C, in the presence of skeleton catalysts Cu—Al, Pd—Al, Co—Al, Ni—Al, Zn—Al and Cu—Zn—Al of Raney-type. Analyses of reaction product were carried out by the method of vapour-, and gas-liquid chromatography using a Willy Giede GCHF 18/2 gas chromatograph. The products were analyzed on two columns. One of them was packed with alumina and used for the analysis of the gaseous products, while the other was packed with  $\beta$ ,  $\beta'$ -oxidipropionitril ether supported on fire brick and used for the analysis of the liquid products. Dry hydrogen was used as carrier gas. The qualitative evaluation was done by means of the control compounds and the retention time, the quantitative analysis was carried out by means of the calibration curves plotted on the basis of planimetry<sup>2</sup>.

<sup>1</sup> XXVII: Acta Chim. Hung. 51, 411 (1967).

<sup>2</sup> The general method of producing catalysts, the description of the apparatus and the way of realization of the experiments have been described in a previous paper [1].

Results of the experiments are shown in Fig. 1—6. The main products of the transformation of propanediol-1,3 on catalysts of Raney-type were found to be propionaldehyde, ethylene, ethanol, propanol, allyl alcohol and water.

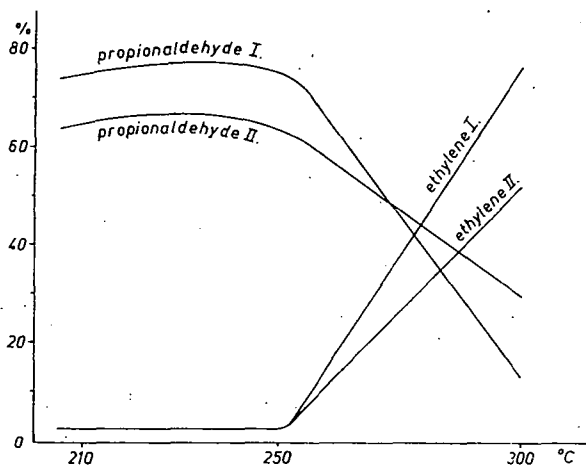


Fig. 1. Transformation of propanediol—1,3 as a function of temperature and rate of feed on a Cu—Al catalyst.

I. propanediol—1,3 4 ml/hour

II. propanediol—1,3 12,5 ml/hour

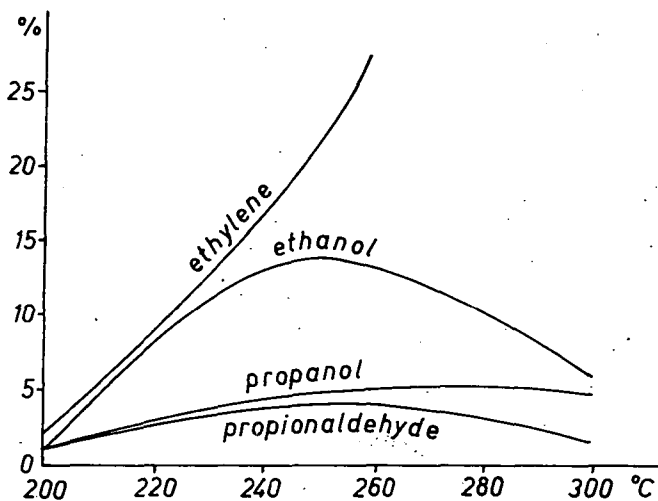


Fig. 2. Transformation of propanediol—1,3 on Pd—Al catalyst as a function of temperature. Rate of feed 4 ml/hour

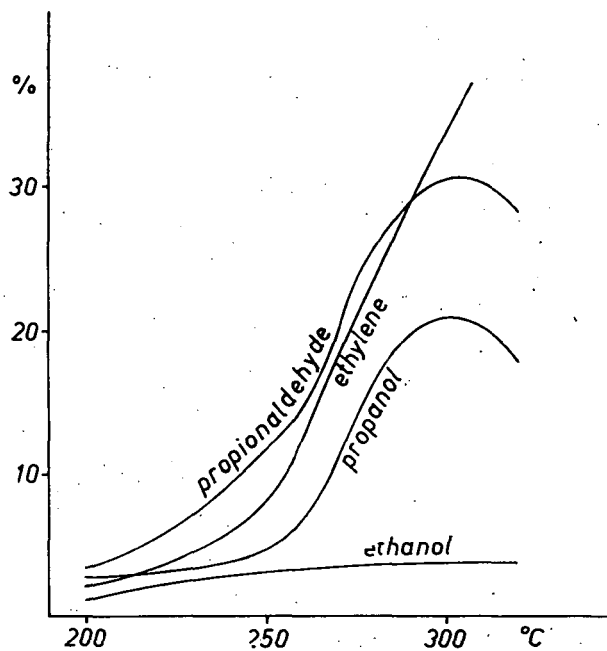


Fig. 3. Transformation of propanediol-1,3 on Co-Al catalyst as a function of temperature. Rate of feed 4 ml/hour

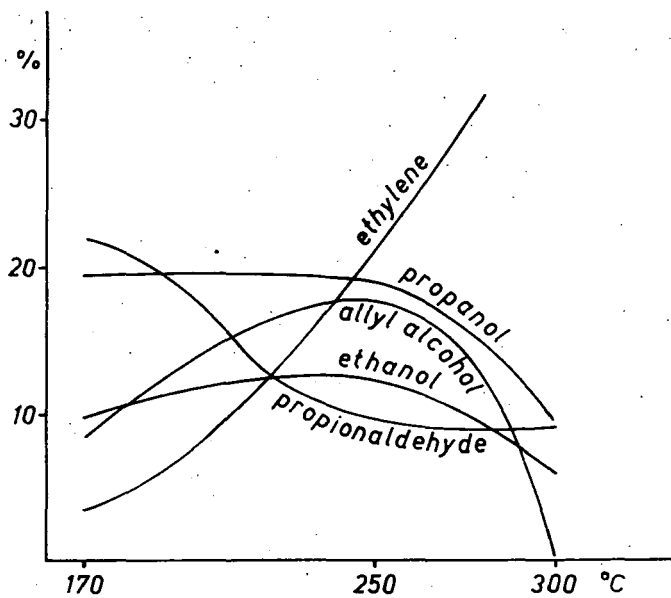


Fig. 4. Transformation of propanediol-1,3 on Ni-Al catalyst as a function of temperature. Rate of feed 4 ml/hour

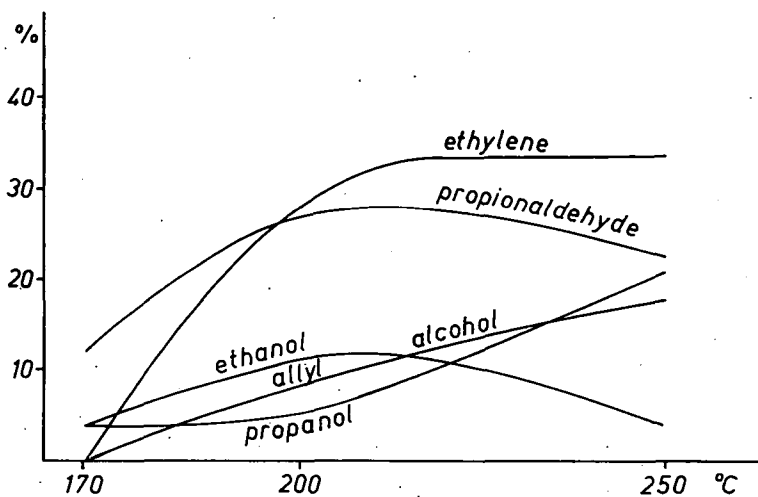


Fig. 5. Transformation of propanediol—1,3 on Zn—Al catalyst as a function of temperature. Rate of feed 4 ml/hour

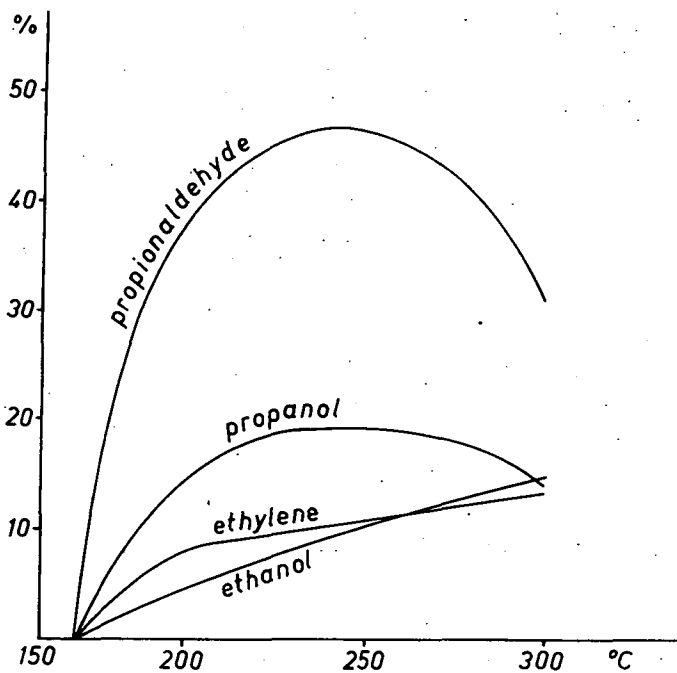


Fig. 6. Transformation of propanediol—1,3 on Cu—Zn—Al catalyst as a function of temperature. Rate of feed 4 ml/hour

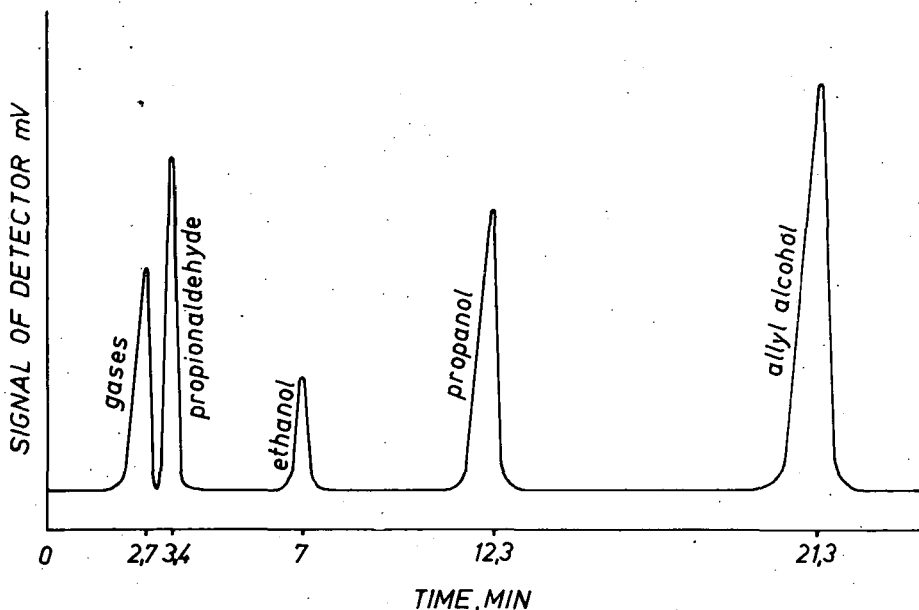
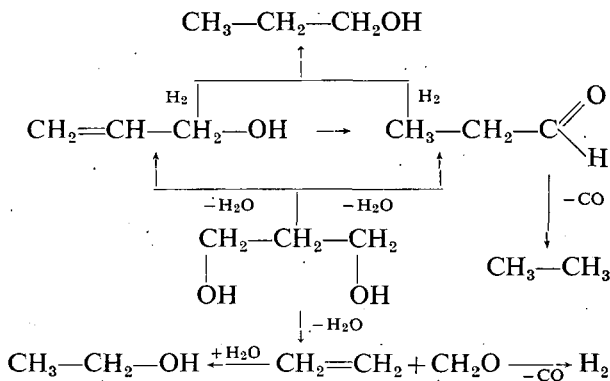


Fig. 7. Chromatogram of products formed at the transformation of propanediol-1,3 on Co—Al, Ni—Al and Zn—Al catalysts.

Conditions of chromatography: solid support: fire brick of 0,2—0,4 mm; partition liquid:  $\beta$ ,  $\beta'$  oxydipropionitril ether (15%); length of column: 1 meter; internal diameter of column: 5 mm; temperature of thermostat: 60 °C; carrier gas: hydrogen (60 ml/min); current of detector: 160 mA; sensitivity: 1 (final deviation 2 mV); sample: 0,005—0,01 ml

The chromatogram of the reaction products is shown in Fig. 7. The transformation of trimethylene-glycol on catalyst of Raney-type, and the formation of its products can be explained by the following reaction scheme:



According to the reaction scheme, the following reactions can be considered as primary processes:

- a) formation of allyl alcohol by 1,2-elimination
- b) formation of propionaldehyde by intramolecular dehydration followed by rearrangement
- c) fragmentation producing formaldehyde and ethylene.

The following secondary processes succeed the primary transformations:

- a) hydrogenation of allyl alcohol and propionaldehyde to produce propyl alcohol
- b) rearrangement of allyl alcohol into propionaldehyde
- c) direct hydration of ethylene to ethanol
- d) decarbonylation of formaldehyde
- e) decomposition of formaldehyde and allyl alcohol also takes place to a certain extent.

For studying both primary and secondary processes the microreactor technique was chosen.

One of the most significant factors is the elucidation of the mechanism of the transformation of trimethylene glycol  $\rightarrow$  propionaldehyde, which can be considered as the main process. Formally the reaction is an 1,3-rearrangement resembling the pinacol rearrangement, which is well known to belong to the 1,2-rearrangements

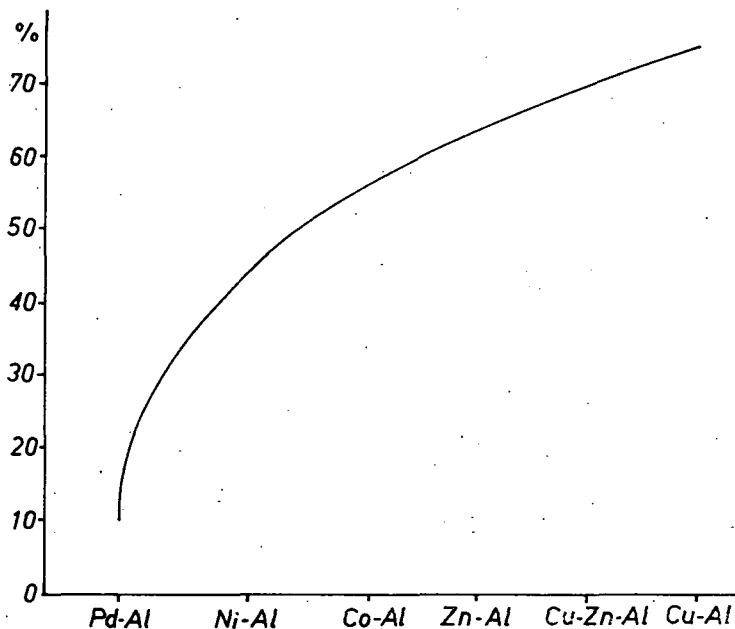


Fig. 8. Total yield of propionaldehyde, allyl alcohol and propyl alcohol formed at the transformation of trimethyleneglycol as a function of the catalysts

generalized in the field of vicinal diols. Propionaldehyde formation was also observed with the transformation of trimethyleneglycol under various experimental conditions (alumina, pumice, sulfuric acid, calcium phosphate) [2—6].

From the curves it can easily be seen that the Cu-Al catalyst has a very good selectivity, a proof being the fact that transformation of trimethyleneglycol to propionaldehyde resulted in an 80% conversion. Selectivities of other catalysts are considerably lower compared to that of the Cu-Al catalyst. Data concerning the activities of various catalysts are summarized in Fig. 8.

Activities of catalysts change in the following order:



The extent of formation of propionaldehyde and allyl-alcohol changes according to a maximum curve as against temperature with most of the catalysts, indicating that the main products further decompose at higher temperatures. Fragmentation becomes predominant as the temperature is increased.

Out of the secondary processes the run of the reaction allyl alcohol  $\rightarrow$  propionaldehyde on metal catalysts of Raney-type is proved [7].

In order to prove the formation of ethanol the analysis was carried out using various column lengths, such as columns of 1, and 3 meters packed with  $\beta$ ,  $\beta'$ -oxydipropionitril aether and one of 2 meters packed with dinonyl phthalate. The formation of ethanol is interpreted with the dehydration of ethylene formed by fragmentation. No data concerning the direct hydration of olefines in the presence of Raney-type catalysts could be found in the literature up to the present time.

#### References

- [1] Bartók, M., Kozma, B.: Acta Phys. et Chem. Szeged 9, 116 (1963).
- [2] Nef, A.: Ann. 335, 206 (1904).
- [3] Rix, M.: Monatsh. 25, 274 (1904).
- [4] Юрьев, Ю. К., И. С. Леви: Доклады АН СССР 78, 725 (1951).
- [5] Юрьев, Ю. К., И. С. Леви: Ж. Общ. Хим. 23, 2047 (1953).
- [6] Фрейдлин, Л. Х., В. З. Шарф: Доклады АН СССР 136, 1108 (1961).
- [7] Фрейдлин, Л. Х., М. Ф. Абидова, А. С. Султанов: Изв. АН СССР хим. наук 1958, 498.

#### ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ И ОРГАНИЧЕСКИХ ОКИСЕЙ. XXVIII

*Изучение превращений триметиленгликоля в паровой фазе на скелетных катализаторах*

*М. Барток, Л. Залотай*

Настоящая работа занимается изучением превращений триметиленгликоля на скелетных катализаторах Cu—Al, Pd—Al, Co—Al, Ni—Al, Zn—Al и Cu—Zn—Al в паровой фазе, в зависимости от температуры и объемной скорости. В процессе дегидратации главными направлениями являются: образование пропионового альдегида в результате перегруппировки и вследствие расщепления образование этилена. Первичные реакции сопровождаются разными вторичными процессами. Для получения пропионового альдегида (выход 76%) оптимальными условиями являются: катализатор Cu—Al, температура 200—250 °C.