

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

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

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The vapour-phase transformation of butanediol-1,3 in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd—Al, Co—Al, Ni—Al, Zn—Al and Cu—Zn—Al as catalysts of Raney-type was investigated at temperatures ranging from 150 to 300 °C. The extent of different reaction paths as the function of catalysts and temperature was studied. Main processes are considered to involve intramolecular dehydration producing butyraldehyde, methyl ethyl ketone, and fragmentation producing propylene. Formation of carbonyl compounds gives a maximum curve against temperature. Fragmentation increases as the temperature is raised. A maximum yield of 55—60% of carbonyl compounds can be obtained in the presence of secondary metals (Zn, Cu—Zn) at a temperature of about 250 °C.

The present paper deals with the transformation of butanediol-1,3 on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd—Al, Ni—Al, Zn—Al and Cu—Zn—Al catalysts of Raney-type, between temperatures ranging from 150 to 300 °C. Transformation of butanediol-1,3 was investigated in a pipe reactor in flow system<sup>2</sup>. Analysis of reaction products was carried out in the same manner as in the case of propanediol [1].

Experimental results are shown in Fig. 1—6. Main products of the transformation of butanediol-1,3 on metal catalysts of Raney-type were butyraldehyde, methyl ethyl ketone, propene and water. The formation of methyl vinyl ketone was also observed with the reaction carried out in the presence of alumina catalyst.

Two characteristic chromatograms are shown in Fig. 7. and 8. Formation of butanediol-1,3 products on the mentioned catalysts can be explained on the basis of the following reaction scheme:

<sup>1</sup> XXVIII: Acta Phys. et Chem. Szeged **14**, 39 (1968).

<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 [2].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst of RB—13 Type prepared by Szerves Vegyipari Kutató Intézet (Budapest) was used.

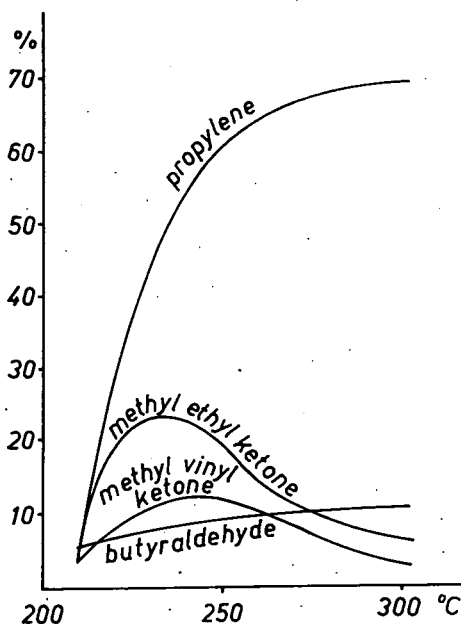
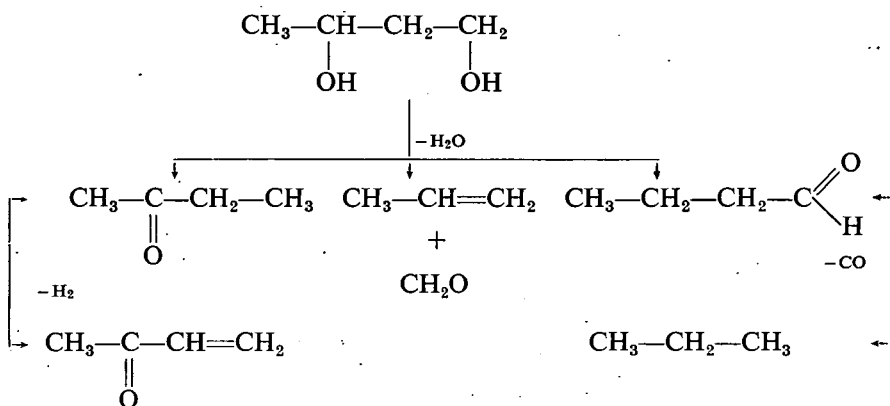


Fig. 1. Transformation of butanediol-1,3 as a function of temperature on alumina catalyst. Rate of feed 4 ml/hour

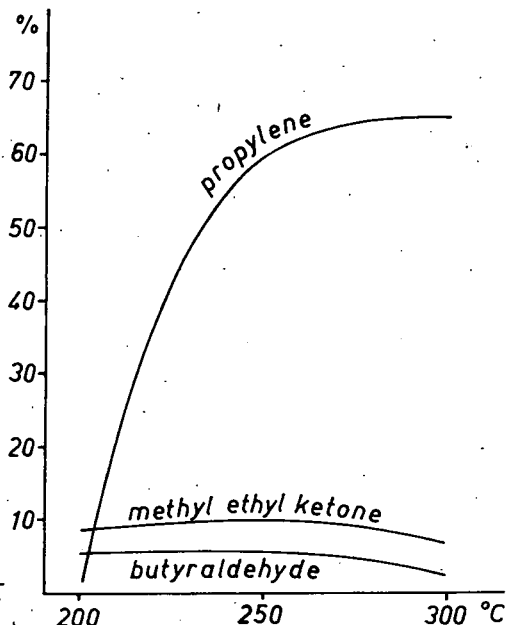


Fig. 2. Transformation of butanediol-1,3 as a function of temperature on Pd-Al catalyst. Rate of feed 4 ml/hour

The formation of butyraldehyde and methyl ethyl ketone as well as the formation of formaldehyde and propene by fragmentation are regarded as primary processes. These primary processes are followed by secondary ones, namely by the decomposition and decarbonylation of formaldehyde and the dehydrogenation of methyl ethyl ketone. Experiments are planned to study the mechanism of primary and secondary processes by means of the microreactor technique. One of the most

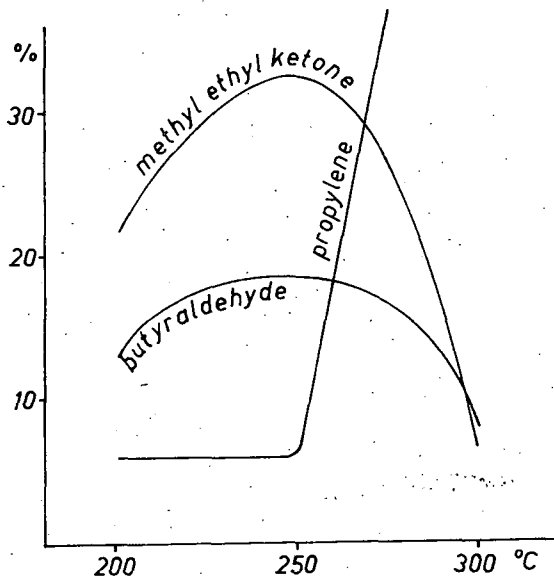


Fig. 3. Transformation of butanediol—1,3 as a function of temperature on Co—Al catalyst. Rate of feed 4 ml/hour

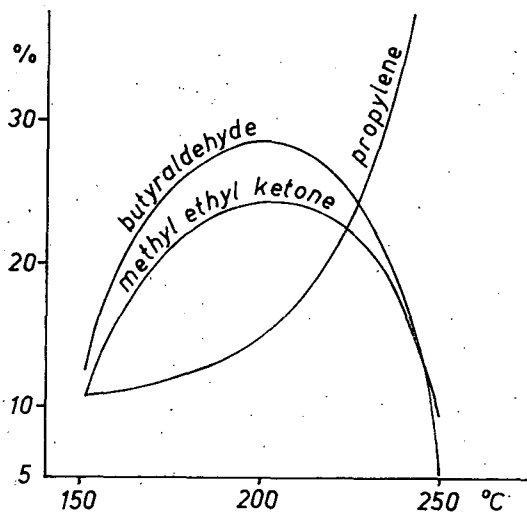


Fig. 4. Transformation of butanediol—1,3 as a function of temperature on Ni—Al catalyst. Rate of feed 4 ml/hour

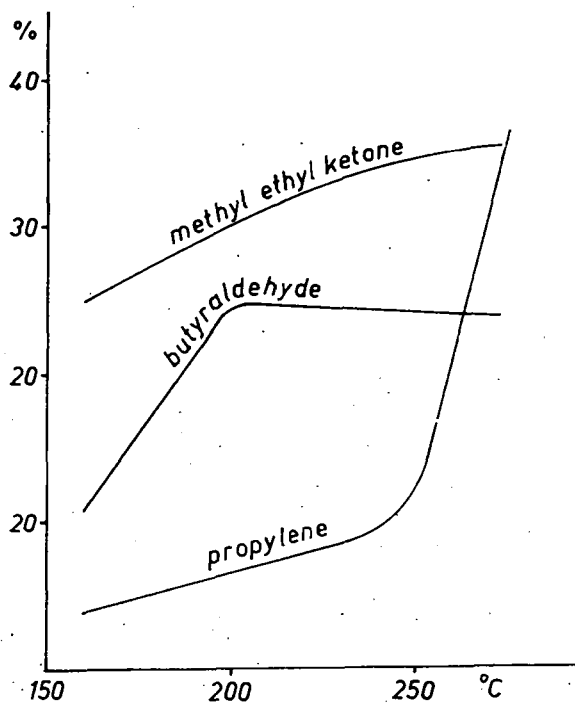


Fig. 5. Transformation of butanediol-1,3 as a function of temperature on Zn-Al catalyst. Rate of feed 4 ml/hour

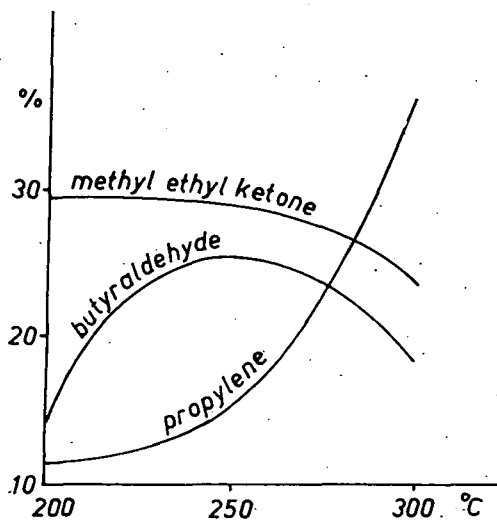


Fig. 6. Transformation of butanediol-1,3 as a function of temperature on Cu-Zn-Al catalyst. Rate of feed 4 ml/hour

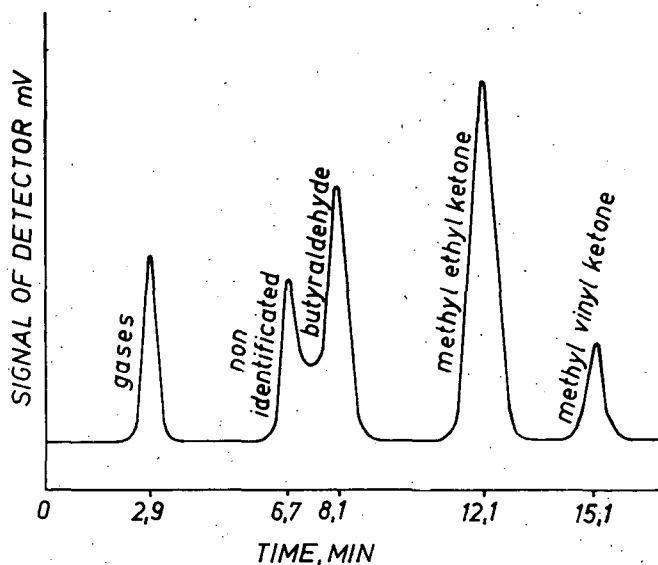


Fig. 7. Chromatogram of products formed at the transformation of butanediol—1,3 on alumina catalyst.

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

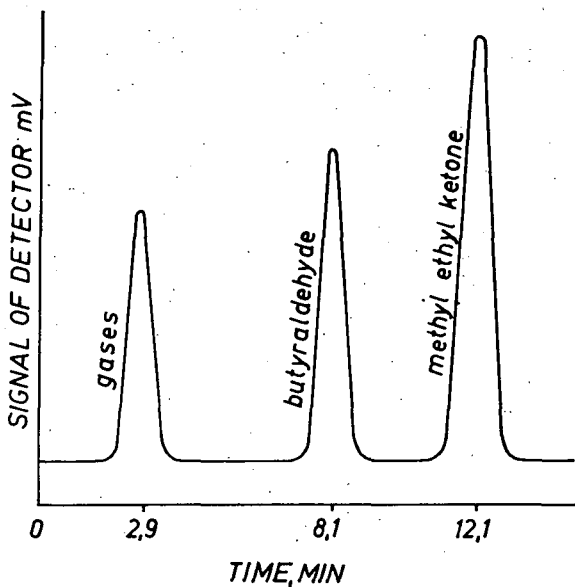


Fig. 8. Chromatogram of products formed at the transformation of butanediol—1,3 on catalysts of Raney-type. Conditions of chromatography were the same as in Fig. 7.

essential tasks is to elucidate the mechanism of the transformation of butane-1,3-diol  $\rightarrow$  butyraldehyde + methyl ethyl ketone, which is considered to be the main process. Formally the process is an 1,3-rearrangement combining with an intramolecular dehydration. From the plots it can easily be seen that the two isomer

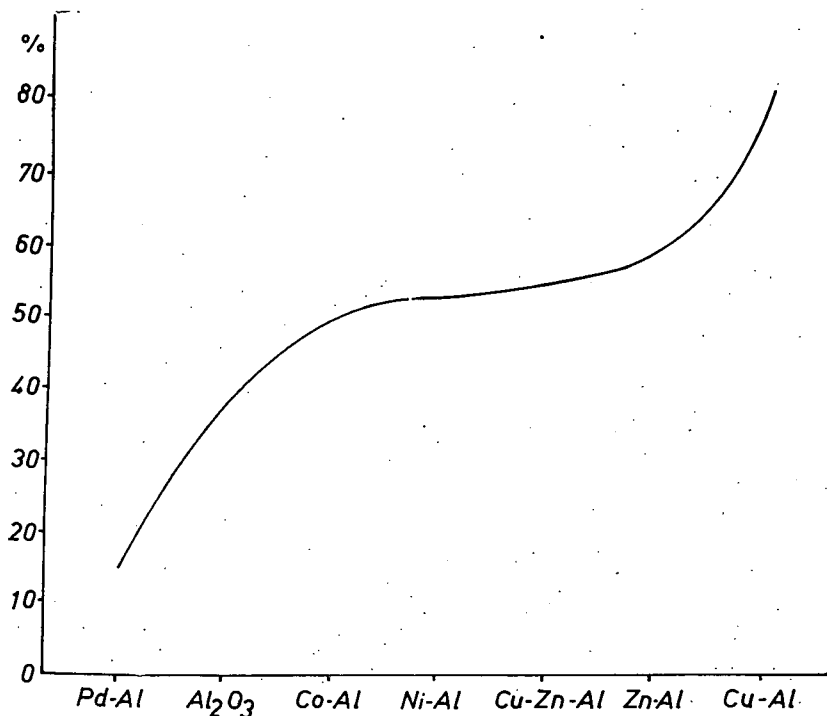


Fig. 9. Total yield of butyraldehyde and methyl ethyl ketone formed at the transformation of butanediol-1,3 as a function of the catalysts

carbonyl compounds are formed with a considerably higher yield and selectivity on metal catalysts of Raney-type than on alumina catalyst. Condensation of varying directions could also be observed in the presence of alumina catalyst, since, as the reaction temperature was raised, the yield of products of high boiling point increased proportionally. Comparing the experimental results obtained in the presence of metal catalysts of Raney-type with those obtained earlier using a Cu—Al catalyst [2] it can be established that the latter catalysis of the reactions of butanediol-1,3  $\rightarrow$  carbonyl compounds proceeds with higher efficiency. Fig. 9. shows the activity of the catalysts. Thus, accordingly the activity of the catalysts changes in the following order: Cu—Al > Zn—Al > Cu—Zn—Al > Ni—Al  $\cong$  Co—Al > Al<sub>2</sub>O<sub>3</sub> > Pd—Al.

The yield of carbonyl compounds gives a maximum curve when plotted against the temperature, indicating a further decomposition of the main products at higher temperatures. With increasing temperature the fragmentation also increases. At the same time it can also be seen that proceeding fragmentation takes place

simultaneously with the formation of carbonyl compounds. Hence, the formation of gaseous products can be explained not only by secondary processes. A similar change of methyl ethyl ketone to butyraldehyde also proves the fragmentation to be a primary process. That is, increasing the temperature not only the yield of butyraldehyde decreases but that of methyl ethyl ketone, too.

Formation of acetaldehyde and ethylene by fragmentation was not observed under the examined experimental conditions. It is interesting to study the yield of methyl ethyl ketone and butyraldehyde as the function of the catalysts. The yield of methyl ethyl ketone was higher in every case except when Ni—Al catalyst was used.

This experimental fact must by all means be taken into consideration when the mechanisms of these reactions are studied, because useful data can be obtained as regards how the catalysts exert their action.

#### References

- [1] Bartók, M., L. Zalotai: Acta Phys. et Chem. Szeged 14, 00 (1968).  
[2] Bartók, M., B. Kozma: Acta Phys. et Chem. Szeged 9, 116 (1963).

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

*Изучение превращений бутандиола-1,3 в паровой фазе на окиси алюминия  
и на скелетных катализаторах*

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Настоящая работа занимается изучением превращений бутандиола-1,3 на окиси алюминия и на скелетных катализаторах Pd—Al, Co—Al, Ni—Al, Zn—Al и Cu—Zn—Al в проточной системе, между 150—300 °С. В процессе дегидратации главными направлениями являются следующие: образование бутирального альдегида и бутанона-2 в результате перегруппировки а вследствие расщепления образование пропилена. Максимальный выход карбонильных соединений (60%) получили на катализаторах Zn—Al и Cu—Zn—Al, около 250 °С.