

Catalytic reactions of pentamethylene and hexamethylene glycols over an iron oxide

Hanna Grabowska^a, Roman Klimkiewicz^a, Józef Wrzyszc^{a,*}, Ludwik Syper^b

^a Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław 2, Poland

^b Institute of Organic Chemistry, Biochemistry and Biotechnology, Technical University of Wrocław, Wrocław, Poland

Received 30 July 1999; received in revised form 13 September 1999; accepted 8 October 1999

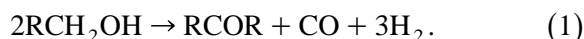
Abstract

Pentamethylene and hexamethylene glycols over a catalyst consisting of iron, silicon, chromium and potassium oxides undergo intramolecular condensation at about 640 K, but considerably different products are obtained: 2,3-dihydropyran and cyclopentanone, respectively. Above 650 K, both glycols undergo intermolecular condensation forming corresponding 5-nonanone and 6-undecanone. Reactions were carried out in a standard flow system under atmospheric pressure in the gas phase. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pentamethylene glycol; Hexamethylene glycol; Ketonization; Iron catalyst

1. Introduction

Primary alcohols over base catalysts undergo bimolecular condensation with simultaneous dehydrogenation and elimination of CO. As a result, there appear ketones according to the general reaction:



Reactions of monohydroxyl alcohols are quite well described [1–3], but far less work has been devoted to catalytic dehydrogenation of polyalcohols in a gas phase over heterogeneous catalysts. From glycerol, over a copper catalyst, there appears acetaldehyde [4]. Ethylene glycol by oxydehydrogenation over silver or copper

catalysts gives glyoxal [5,6]. According to Montasier et al. [7], Ru, Ni, Rh and Ir catalysts hydrogenolyze, under hydrogen, both C–C and C–O bonds of polyols to hydrocarbons, while copper-based catalysts convert selectively sorbitol to glycerol. There are also papers presenting the results of dehydration of cyclic alcohols with ring transformation [8–10] and dehydration of pentamethylene and hexamethylene glycols [11,12]. Recently, Leite et al. [13] have investigated the transformations in cyclodehydration reactions of 4-hydroxybutanal and tetramethylene glycol to 2,3-dihydrofuran and tetrahydrofuran in the presence of pretreated porcelain.

Studying the ketonization of normal alcohols over an iron catalyst, it was indicated that this contact exhibited high activity and selectivity [14]. It was of interest to study the reactivity of glycols containing hydroxyl groups at the ends

* Corresponding author. Fax: +48-71-344-1029.

E-mail address: wrzyszc@int.pan.wroc.pl (J. Wrzyszc).

of carbon chain, especially pentamethylene and hexamethylene glycols.

2. Experimental

Reactions were carried out in the gas phase under atmospheric pressure in a typical flow system with a fixed bed ($V_{\text{cat.}} = 3.0 \text{ cm}^3$) within the temperature range of 563–663 K and with load of 1.0 h^{-1} . The raw material was fed in a continuous manner from the reactor's top using a micropump. The catalyst was prereduced with methanol at 473 K for 1 h, then the substrate was fed. The experiments were performed in the function of increasing temperature, collecting the reaction products at chosen temperatures after the stationary equilibrium set in, after approximately 1 h. After a series of experiments, the catalyst was regenerated with air at 743 K. The condensed products were analysed using gas chromatography and identified by mass spectroscopy (HP MSD 59). The gas chromatograph HP 6890 was equipped with a FID detector and a capillary column HP-5 ($30 \text{ m} \times 0.32 \text{ mm}$) filled with phenyl methyl silicone.

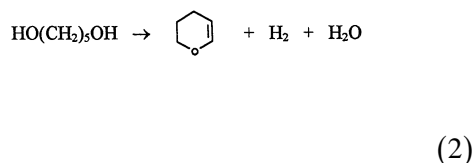
The catalyst consisted of a mixture of iron, silicon, chromium and potassium oxides in molar ratio of 100:2:1:0.1. Silicon and chromium oxides prevent sintering while potassium acts as an activator. The catalyst was obtained by coprecipitation at room temperature from an aqueous solution of iron and chromium nitrates and sodium silicate with ammonia solution (1:1) until pH 7 was reached. The obtained suspension was filtered off and washed out with distilled water to remove nitrate ions, then impregnated with the aqueous solution of potassium carbonate. The precipitate was dried, ground and palletized with a 3% addition of graphite. The pellets were calcinated in air at 743 K and crushed into 0.6–1.2 mm grain size. X-ray diffraction showed that the fresh catalyst was $\alpha\text{-Fe}_2\text{O}_3$. Its specific surface area (nitrogen BET method) was $60 \text{ m}^2/\text{g}$. After the usage, the structure of the catalyst changed to Fe_3O_4 of

S_{BET} of around $40 \text{ m}^2/\text{g}$. More specific information on the physico-chemical properties of this catalyst had been described in greater details earlier [15].

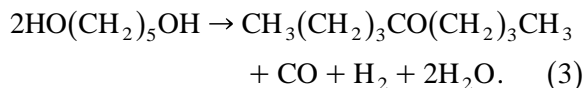
3. Results and discussion

Table 1 presents the results of glycol transformation.

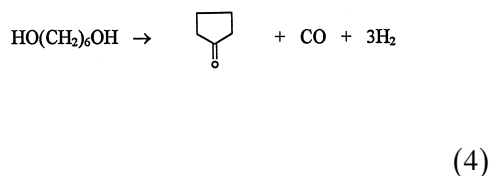
Pentamethylene glycol undergoes intramolecular condensation to dihydropyran:



At higher temperatures, as a result of dehydration, simultaneous dehydrogenation and hydrogenation [16] there appears *n*-pentanal which is condensed to *n*-pentyl *n*-valerate and next dehydrogenated to 5-nonanone:



Hexamethylene glycol undergoes intramolecular condensation to cyclopentanone at temperatures about 640 K:



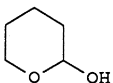



At higher temperatures, like from pentamethylene glycol, there appear *n*-heksanal, *n*-hexyl *n*-caproate and, as a final product, 6-undecanone.

At lower temperatures, both glycols undergo entropically positive changes of intramolecular condensation similarly as it is observed in reactions carried out in a homogenous phase with this type of substrates [17]. However, considerably different products are obtained: unsaturated

Table 1

Results of pentamethylene and hexamethylene glycols and 2-hydroxytetrahydropyran conversion over an iron catalyst

Substrate	Cyclic ketone	Cyclic ether	Normal ketone
HO(CH ₂) ₅ OH	-		5-nonanone max. yield = 45.2% at 663 K
		max. yield = 25.5% at 643 K	
HO(CH ₂) ₆ OH		-	6-undecanone max. yield = 52.0% at 663 K
	max. yield = 18% at 643 K		
	-		-
		max. yield = 81.0% at 563 K	

ether from pentamethylene glycol and cyclic ketone from hexamethylene glycol. At higher temperatures, the products disappear because reactions of forming aldehydes and products of intermolecular condensation become dominant.

Table 2 presents the post-reaction mixtures composition obtained as a result of pentamethylene glycol conversion.

Table 2
Results of pentamethylene glycol transformation

Reaction temperature (K)	643	653	663
Conversion of pentamethylene glycol (%)	92.5	96.0	97.5
Product components (%):			
Dihydropyran	25.5	22.0	8.0
5-nonanone	1.0	25.0	45.2
<i>n</i> -pentanol	47.5	22.5	14.4
<i>n</i> -pentanal	8.3	6.9	3.0
<i>n</i> -pentyl <i>n</i> -valerate	4.8	2.1	1.0
Pentene	4.4	8.5	12.6
Others	1.0	9.0	13.3

In the case of hexamethylene glycol, an analogous composition of products was observed excluding cyclopentanone.

To test if the primary reaction in glycols, which initiates the whole process, is the dehydrogenation reaction of one of hydroxyl group with the hydroxyaldehyde as a product, a substrate of 2-hydroxytetrahydropyran, being a cyclic tautomer of 5-hydroxypentanal, was used.

As a result of the reaction, one product was obtained — 2,3-dihydropyran — which resulted from the dehydration of 2-hydroxytetrahydropyran. In the reaction conditions, it was a sustainable product and did not undergo further transformations. In the products of the reaction of pentamethylene glycol also appeared 2,3-dihydropyran. It was an evidence that the glycol, at least partially, underwent dehydrogenation to hydroxyaldehyde. The reaction that was assumed as likely to appear, i.e., dehydrogenation

of 2-hydroxytetrahydropyran to δ -valerolactone, did not occur.

4. Conclusions

Pentamethylene and hexamethylene glycols over an iron catalyst, to some extent, undergo intramolecular reactions and, to far higher extent, intermolecular condensation, typical for monohydroxyl alcohols. Intramolecular condensation of pentamethylene glycol consists only in dehydration and dehydrogenation without breaking C–C bond, while intramolecular condensation of hexamethylene glycol is an analogous reaction to intermolecular ketonization of normal alcohols.

References

- [1] V.I. Komarewsky, J.R. Coley, *J. Am. Chem. Soc.* 63 (1941) 3269.
- [2] P.H. Emmett, P. Sabatier, in: *Catalysis Then and Now*, Franklin Publ., New York, 1965, p. 650.
- [3] M. Kraus, in: G. Ertl, H. Knoezinger, J. Weitkamp (Eds.), *Handbook of Heterogeneous Catalysis 5* VCH, Weinheim, 1997, p. 2159.
- [4] B.N. Dolgow, in: *Die Katalyse in der Organischen Chemie*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1963, p. 271.
- [5] P. Gallezot, S. Tretjak, Y. Christidis, G. Mattioda, A. Schouteeten, *J. Catal.* 142 (1993) 729.
- [6] A.J. Capote, R.J. Madix, *J. Am. Chem. Soc.* 111 (1989) 3570.
- [7] C. Montassier, D. Giraud, J. Barbier, in: *Studies in Surface Science and Catalysis*, M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier, G. Perot (Eds.), *Heterogeneous Catalysis and Fine Chemicals* Elsevier, Amsterdam, 41 1988, p. 165.
- [8] H. Pines, S.M. Brown, *J. Catal.* 20 (1971) 74.
- [9] C.L. Wilson, *J. Am. Chem. Soc.* 69 (1947) 3004.
- [10] A. Misono, T. Osa, Y. Sanami, *Bull. Chem. Soc. Jpn.* 41 (1968) 2447.
- [11] Y. Inoue, S. Deguchi, T. Hakushi, *Bull. Chem. Soc. Jpn.* 53 (1980) 3031.
- [12] L.T. Scott, J.O. Naples, *Synthesis* (1973) 209.
- [13] L. Leite, A. Lebedevs, V. Stronkus, M. Fleisher, *J. Mol. Catal. A: Chem.* 114 (1999) 323.
- [14] J. Wrzyszczyk, H. Grabowska, R. Klimkiewicz, L. Syper, *Catal. Lett.* 54 (1998) 55.
- [15] H. Grabowska, W. Mišta, L. Syper, J. Wrzyszczyk, M. Zawadzki, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 1562.
- [16] E.K. Rideal, H.S. Taylor, in: *Catalysis in Theory and Practice*, Macmillan, London, 1926, p. 287.
- [17] J. March, in: *Advanced Organic Chemistry*, Wiley, New York, 1992, p. 208.