

THE REACTION OF ETHYLENE OXIDE WITH ALIPHATIC ALCOHOLS IN THE PRESENCE OF ZEOLITES Y AS CATALYSTS

Bogdan Burczyk, Florian Kukla

Institute of Organic Technology and Plastics,
Technical University, Wrocław 50-370, Poland

Studies have been carried out on ethylene oxide addition to straight-chain aliphatic alcohols: ethanol, butanol, hexanol, octanol and decanol. Active forms of zeolite Y were used as catalysts. The qualitative and quantitative composition of reaction products has been determined.

Studies presented in this paper concern the synthesis of non-ionic surface active compounds, particularly of oxyethylenated aliphatic alcohols. It is well known that surface active compounds which include the anionic, cationic, ampholytic and non-ionic compounds are being now widely used in practice. The largest amounts of these substances are used in household in the form of various agents for washing and cleaning. They find also increasingly wide use in industry as wetting agents, emulsifiers, dispersing agents etc.

The group of non-ionic surface active compounds includes mainly the oxyethylenated alcohols, oxyetylenated alkylphenols, fatty acid esters with polyoxyethyleneglycols, polyalcohols esterified with fatty acids and their oxyethylenated derivatives. From the point of view of quantity the products based on alcohols represented in 1975 the most important group of these compounds [1]. Among other factors this is due to the fact that the production of aliphatic alcohols (fatty alcohols, Alfols, Oxo-alcohols) as well as of ethylene oxide was increasing in recent years and there are growth tendencies for near future. The discussed products have a low toxicity against aquatic organisms and are readily biodegradable. These factors, in addition to several other useful properties, favour the increasingly wide use of these products.

Oxyethylenated alcohols are prepared by reacting alcohols with ethylene oxide in the presence of acidic or basic catalysts. The addition of ethylene oxide to alcohols in the presence of basic catalysts (e.g. MeOH,

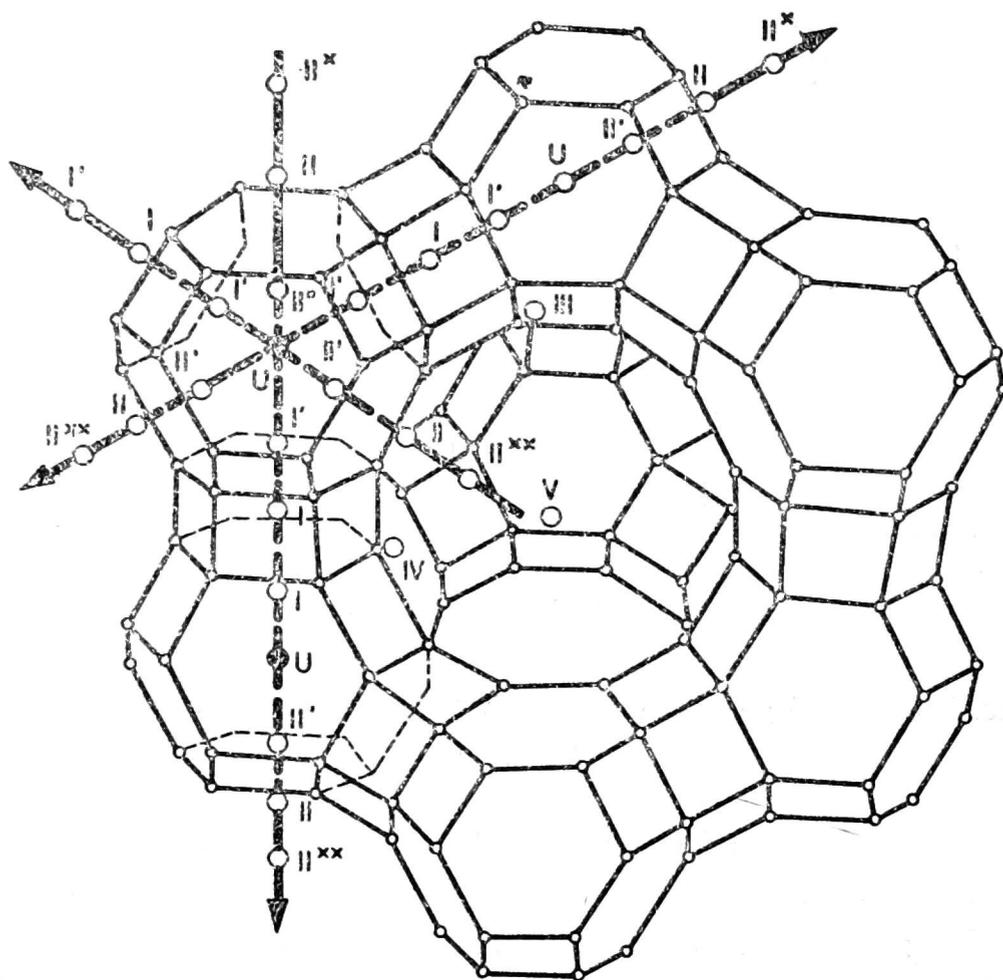


Fig. 3. Crystalline structure of faujasite

were conducted in a standard glass apparatus under normal pressure by passing gaseous ethylene oxide into a suspension of catalyst in alcohol. The rate of flow of ethylene oxide was regulated with a valve. The reactions were carried out at elevated temperatures maintained within $\pm 1^\circ\text{C}$. The reaction was discontinued when the desired substrate conversion was achieved, as given by the molar ratio, the product was then cooled, the weight was determined and samples were taken for chromatographic analysis.

The qualitative and quantitative composition of reaction products were determined by gas-liquid chromatography using a Perkin-Elmer F 11 apparatus equipped with flame-ionizing detector. Glass columns 1 m ϕ 3 mm were used with two kinds of packing: 20% Carbowax M20 on Chromosorb G 60/80 mesh and 8% Apiezon L on Gas Chrom P 80/100 mesh.

The polyglycol content in reaction products was determined by the extraction method described by Blomyer [3].

RESULTS

The reaction of ethylene oxide addition to alcohols were examined at molar ratios equal about 1 : 1. Other parameters are presented in Table 1 which includes also the conversion of alcohol used. The results

Table 1

Reaction conditions and conversion of aliphatic alcohols

No.	Alcohol C_nOH	Mol ratio of substrates EO^*/C_nOH (mol/mol)	Amount of catalyst (g/mol)	Reaction temperature (°C)	Reaction time (h)	Conversion
						$\left[\frac{m_0 - m}{m_0} \times 100 \right]$
1	C_2OH	1.03	12.5	70	3.0	68.1
2	C_4OH	1.01	20.0	100	1.8	61.5
3	C_6OH	1.10	20.0	100	3.0	52.6
4	C_8OH	1.20	25.0	100	3.0	40.8
5	$C_{10}OH$	0.87	25.0	100	4.0	28.0

* Ethylene oxide.

indicate that the conversion decreases with increasing length of hydrocarbon chain of alcohols. This relation is shown graphically in Fig. 4. This fact can be explained by the different relative acidities of individual alcohols, decreasing with increasing length of the hydrocarbon chain in alcohols. These results are in accord with those reported by Svets and T'ukova [9]. These authors have found that the conversion

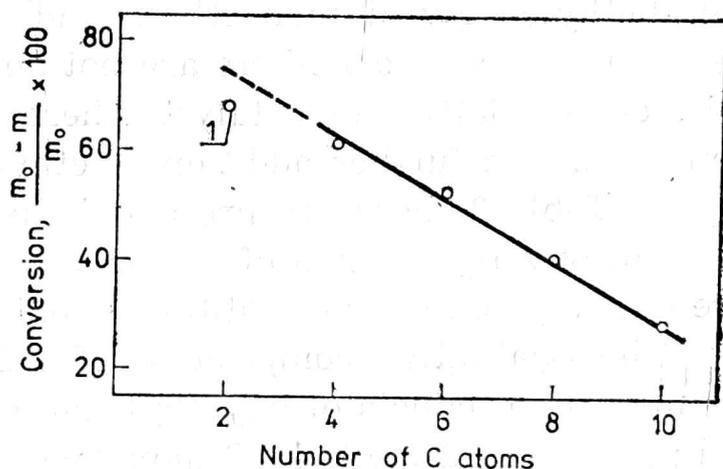


Fig. 4. The relation between alcohol conversion and the number of carbon atoms in hydrocarbon chain, for conditions as given in Table 1

of alcohols in reaction with ethylene oxide decreases with the acidity of alcohols. On the other hand, Barrer and Oei [2] in their studies of polymerization of alkyl vinyl ethers on the active forms of zeolite Y have established that the dimensions of alkyl groups do not determine the kinetics of polymerization. Our results are essentially in accord with this observation.

The composition of products of ethylene oxide addition to investigated alcohols is presented in Table 2 and in graphical form in Fig. 5. In the products of ethylene oxide addition to ethanol, butanol and he-

Table 2

The composition of products of ethylene oxide addition to aliphatic alcohols

No.	Alcohol C_nOH	Composition of reaction mixture, weight — %				
		C_nOH	C_nOE_1	C_nOE_2	C_nOE_3	total
1	C_2OH	16.1	51.2	19.6	6.0	92.9
2	C_4OH	23.4	46.7	15.6	3.8	89.5
3	C_6OH	32.1	44.0	8.0	1.1	85.2
4	C_8OH	42.8	34.5	6.7	—	84.0
5	$C_{10}OH$	57.8	25.9	3.1	—	86.8

C_nOE_1 — ethylene glycol alkyl ether.

C_nOE_2 — diethylene glycol alkyl ether.

C_nOE_3 — triethylene glycol alkyl ether.

xanol there was found the presence of the monoethers of ethylene-, diethylene- and triethyleneglycol whereas only the monoethers of ethylene glycol and diethylene glycol were found in the products of oxyethylenation of octanol and decanol. We never found any higher homologues, i.e. the products of a higher degree of oxyethylenation which could be expected from the Poisson distribution for the investigated molar ratio of substrates. We have thus confirmed our earlier observation of the sieve effect of zeolite catalysts in the oxyethylenation of *n*-butanol under various conditions [8]. This effect results from the fact that the molecules of diethyleneglycol monoethers and sometimes even the molecules of ethylene glycol monoethers are not able, for steric reasons, to enter into the crystal lattice of catalyst where there are the active acid centres on which the further addition of ethylene oxide could take place.

In Table 3 there are presented the side-products formed in the process of oxyethylenation of alcohols in the presence of zeolite *H—Y*. There is also given their quantitative content in reaction products.

The qualitative composition of side-products is very similar. Thus, among the products of oxyethylenation of all alcohols there were found: acetaldehyde, 2-methyl-1,3-dioxolane, *p*-dioxane and polyglycols. In addition, diethyl ether was detected in the products of oxyethylenation of ethanol. This product is formed by ethanol dehydration on catalyst. However, no symmetrical ethers were formed among reaction products of higher alcohols. This observation is in accord with the results of Bryant and Kranich concerning the dehydration of ethanol and *n*-butanol in the presence of synthetic zeolites as catalysts [4]. In ethanol dehydration the major product, in addition to ethylene, was the diethyl ether whe-

Table 3

The content of side-products in oxyethylenated aliphatic alcohols

No	Alcohol C _n OH	Content of side-products weight — %					total
		(C ₂ H ₅) ₂ O	CH ₃ CHO + EO*	2-methylo- -1,3-dioxo- lane	p-Dioxane	polygly- cols	
1	C ₂ OH	1.1	2.6	0.8	traces	2.6	7.1
2	C ₄ OH	3.2**	0.6	0.8	2.1	3.8	10.5
3	C ₆ OH	—	1.2	2.7	2.1	3.8	9.8
4	C ₈ OH	—	1.7	3.9	3.8	6.6	16.0
5	C ₁₀ OH	—	0.9	1.0	4.6	6.7	13.2

* Ethylene oxide.

** Amount of 2-propyl-1,3-dioxolane.

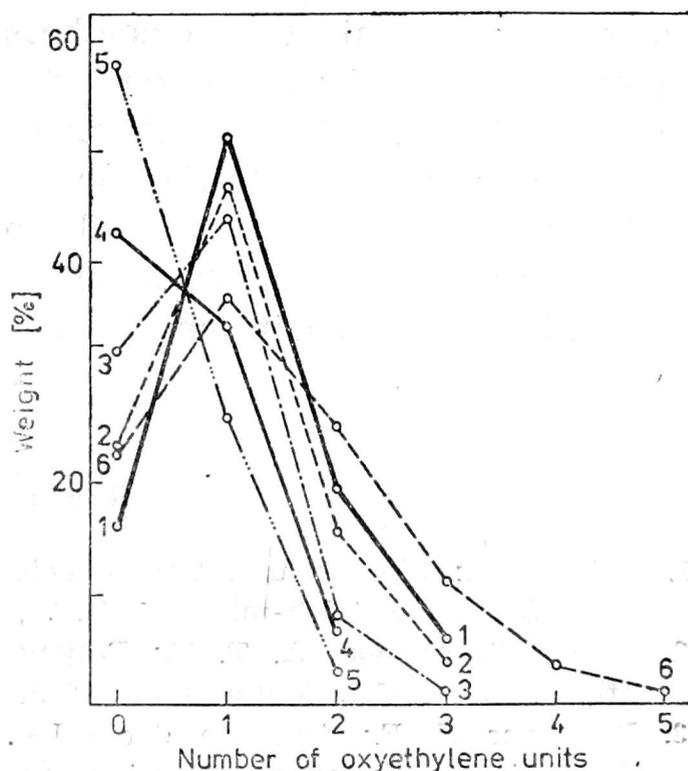


Fig. 5. Distribution curves of homologous monoethers present in oxyethylenation products of ethanol (1), *n*-butanol (2), *n*-hexanol (3), *n*-octanol (4) and *n*-decanol (5). Curve (6): Poisson distribution

reas the dehydration of *n*-butanol produced a mixture of butenes but no dibutyl ether. According to these authors such results demonstrate that the dehydration of alcohols takes place within the crystal lattice of zeolites where there is no possibility of formation of ethers of higher alcohols with larger dimensions of molecules.

Interesting is also the fact that 2-propyl-1,3-dioxolane is present in the products of oxyethylenation of *n*-butanol only. This indicates that there is an oxidation of *n*-butanol to butyraldehyde in the presence of the zeolite used. Subsequent reaction of this aldehyde with ethylene oxide yields the cyclic acetal in question [6].

The amount of side-products of oxyethylenation of alcohols in the

presence of active forms of zeolite Y depends mainly on temperature and molar ratio of substrates and is less dependent on the amount of catalyst. Their total content is higher than the content of analogical products formed when protonic acids or Lewis acids are used as catalysts.

CONCLUSIONS

The following conclusions can be drawn on the basis of obtained results:

1. The active forms of zeolites Y obtained by thermal decomposition of ammonium forms at about 560°C are able to catalyze the reaction of ethylene oxide addition to aliphatic alcohols.

2. The reaction products of ethylene oxide with ethanol, butanol and hexanol contain the monoethers of ethylene-, diethylene- and triethylene glycols whereas the reaction products of octanol and decanol contain only the ethers of ethylene glycol and diethylene glycol. This phenomenon is related to the sieve effect of the zeolite catalyst.

3. The conversion of alcohols in reaction with ethylene oxide and the molar yield of alkyl monoethers of polyoxyethylene glycols decrease with increasing chain length with concomitant increase of the amount of side-products.

REFERENCES

1. Asinger F.: *Chemie und Technologie der Herstellung nichtionischer Tenside, Fette-Seifen-Anstrichmittel*, 1973, 75, 559.
2. Barrer R. M., Oei A. T. T.: *Polymerization with Zeolite Catalysts II. Vinyl Ethers Over H-Mordenite and H-Y*, *J. Catal.*, 1974, 34 (1), 19.
3. Blomeyer K. F.: *Arbeiten der C.I.A. unter besonderer Berücksichtigung der Analytik nichtionogener Tenside, Fette-Seifen-Anstrichmittel*, 1969, 71, 240.
4. Bryant D. E., Kranish W. L.: *Dehydration of Alcohols over Zeolite Catalysts*, *J. Catal.*, 1967, 8, 8.
5. Burczyk B., Kukla F.: *Zastosowanie zeolitów jako katalizatorów w niektórych reakcjach związków organicznych*, in: *Zeolity syntetyczne i ich zastosowanie w katalizie*, Ossolineum, Wrocław 1974.
6. Burczyk B., Kukla F.: *Addition of Ethylene Oxide to n-Butanol in the Presence of Y Zeolite Catalysts*, *J. Catal.*, (in press).
7. Schick M. J.: *Nonionic surfactants*, Dekker, New York 1967.
8. Schoenfeldt N.: *Surface Active Ethylene Oxide Adducts*, Pergamon Press, Oxford 1969.
9. Svets W. F., T'ukova O. A.: *Kinetika i stereochemia reakcji α -okisej so spirtami pri katalizie ftoristym borom i chlornoj kislostoj*, *Žur. Org. Chim.*, 1971, 7, 1842.
10. Venuto P. B., Landis P. S.: *Organic Catalysis over Crystalline Aluminosilicates*, in: *Advances in Catalysis*, vol. 18, p. 259, Academic Press, New York 1968.

B. Burczyk, F. Kukla

REAKCJA TLENKU ETYLENU Z ALIFATYCZNYMI ALKOHOLAMI
W OBECNOŚCI ZEOLITÓW Y JAKO KATALIZATORÓW

Streszczenie

W ramach prac nad syntezą niejonowych związków powierzchniowo czynnych zbadano reakcje przyłączania tlenku etylenu do alkoholi alifatycznych: etanolu, *n*-butanolu, *n*-heksanolu, *n*-oktanolu i *n*-dekanolu w obecności aktywnych form zeolitu Y, zawierających centra kwasowe typu Broensteda i Lewisa. Reakcje prowadzono sposobem periodycznym, wprowadzając gazowy tlenek etylenu w ilości 1 mola na mol alkoholu do zawiesiny katalizatora w alkoholu, w zakresie temperatur 50-140°C, w ciągu 1-5 godzin. Produkty reakcji stanowiły mieszaninę monoeterów alkilowych glikolu mono-, dwu- i trójetylenowego oraz związków, będących produktami ubocznymi tej reakcji. Wśród ostatnich zidentyfikowano: aldehyd octowy, *p*-dioksan, 2-metylo-1,3-dioksolan i polioksyetylenoglikole; w produktach oksyetylenowania etanolu występował ponadto eter dwuetylowy, a w produktach oksyetylenowania *n*-butanolu 2-propylo-1,3-dioksolan.

Б. Бурчик, Ф. Кукля

РЕАКЦИЯ ОКИСИ ЭТИЛЕНА С АЛИФАТИЧЕСКИМИ АЛКОГОЛЯМИ
В ПРИСУТСТВИИ ЗЕОЛИТОВ КАК КАТАЛИЗАТОРОВ

Резюме

В рамках трудов по синтезу неионных поверхностно-активных соединений исследовали реакцию присоединения окиси этилена к алифатическим спиртам: этанолу, *n*-бутанолу, *n*-гексанолу, *n*-октанолу и *n*-деканолу в присутствии активных форм цеолита у содержащих кислотные центры типа Брэнстеда и Люиса. Реакции проводили периодическим способом, вводя газообразную окись этилена в количестве 1 моля на моль спирта во взвесь катализатора в спирте в пределах температур 50—140°С на протяжении 1—5 часов. Продукты реакции составляли смесь алкиловых моноэфиров моно-, ди- и триэтиленового гликоля и соединений являющихся побочными продуктами этой реакции. Среди последних были идентифицированы: уксусный альдегид, *n*-диоксан, 2-метило-1,3-диоксолан и полиоксиэтиленогликоли; среди продуктов оксиэтиленования этанола выступал сверх того диэтиловый эфир, а среди продуктов оксиэтиленования *n*-бутанола — 2-пропило-1,3-диоксолан.