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SYNTHESIS OF MIXED DIESTERS OF ETHYLENEGLYCOL

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The etherification reaction of ethyleneglycol with aliphatic saturated acids was studied and synthesized proper monoethers of ethyleneglycol. It was found that among the used various catalysts the most effective was turned out heterocatalyst of KU-2-8 H form. On the bases of obtained oxyethers were synthesized mixed diesters of saturated and acrylic acids that are new monomers

Key words: *etherification, monoethers, diesters, saturated acids, formic acid, acetic acid, propionic acid, butyric acid, ehtyleneglycol, acrylic acid, hydroquinone*

The recent years the acrylic monomers are successfully applied for obtaining valuable polymer materials as superglues, in preparing of artificial dental prostheses, optical lenses, in medicine for covering medicinal preparations [1-3]. On the bases of monomers are obtained polymers that used as typographic paints, computers' monitors, as well as lenses that are the UV-raysproof.

At present research with the purpose of synthesizing novel reactive monomers, at the first stage we have conducted etherification of saturated aliphatic acids (SAA) with ethyleneglycol (EG) and synthesized monoethers on scheme:

$$R\text{-}COOH + HO\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow[-H_2O]{} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$

At the second stage, the obtained hydroxyethylethers (HOEE) by the acrylic acid (AA) etherification were changed to the mixed diesters (MDE):

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH + CH_2{=}CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH \xrightarrow[-H_2O]{} R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH{=}CH_2$$

During the conducting of 1st and 2nd reactions for obtaining MDE we applied various homo- and heterogeneous catalysts: H_2SO_4, H_3PO_4, para-TSA (para-toluenesulfonic-acid), KU-2 H, KU-2-8 H (ion-exchange acids) and NSA (naphthaline sulfonic-acid).

Among them the most efficient and technological, easy realizable was heterogeneous catalyst - ion-exchange resin - KU-2-8 of H-form. Therefore, the etherification reaction of saturated acids (SA) with EG was carried out in presence of mentioned catalyst. For ascertainment its optimal quantity in reactionary medium to the yield of 2-hydroxyethylformate (HOEF), was conducted a series of experiments on the example of etherification of EG with formic acid (FA) and determined its optimal quantities shown in table 1.

Table 1. The influence of quantity of catalyst KU-2-8 H-forms to the yield of HOEF (benzene of 100 g., temperature of 80-85^{0}C, time 4 h.)

Cat. KU-2-8 H, %	Initial compounds, g		Obtained	
	EG	FA	2-hydroxyethylformate	
			g	%
3.0	62.0	46.0	76.8	85.4
4.0	62.0	46.0	81.0	90.0
5.0	62.0	4.0	87.7	97.5
6.0	62.0	4.0	86.4	96.0
7.0	62.0	4.0	84.9	90.4

As seen from the obtained data, the yield of 2-oxyethylformate greatly depends on the quantity of catalyst KU-2-8 of ′H-form as in mass of 5% on EG the HOEF yield increases (reaches) up to 97.5 %, and the further increase of its quantity in reactionary medium causes the decrease of target products to 90.4%.

During the obtaining of other exponents of monoethers of fatty acids of ethyleneglycol was also applied KU-2-8 of H-form catalyst of 5% to the EG mass. The obtained data are shown in Table 2. Besides was used of fatty acids: acetic (AA), propionic (PA) and n-butyric acid (NBA).

Table 2. The influence of quantity of catalyst KU-2-8 to the yield of HOEF (benzene of 100g., temperature of 80-85^{0}C, time 4 h.)

Initial compounds, g.		Cat. KU-2-8 H, %	Obtained	
SA	EG		Structure	%
AA-60.0	62.0	3.1	CH_3-COO-CH_2-CH_2-OH	96.0
PA-74.0	62.0	3.1	CH_3-CH_2-COO-CH_2-CH_2-OH	94.5
NBA-88.0	62.0	3.1	CH_3-CH_2-CH_2-COO-CH_2-CH_2-OH	92.8

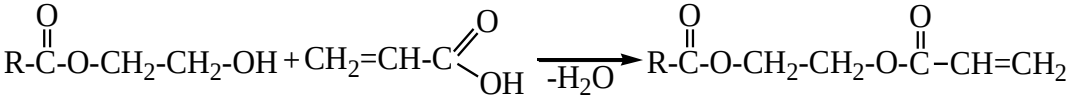
From the Table 2 is seen that in the etherification of saturated acids AA, PA, NBA with EG in presence of catalyst KU-2-8 of H-form the yield of hydroxyethyl esters are from 92.8 to 96.0%. It means that by the increase of mol. mass of saturated acids from FA to NBA the yield of EG monoethers decreases. Apparently, by the increase of SA mol. mass the decrease of dissociation degree negatively affects the yield of HOEF.

By the chromatography analyses was determined the degree of purity of synthesized monoethers that are 98.7 - 99.1 %. In this purity was defined physical-chemical constants obtained EG monoethers which are shown in table 3.

Table 3. Physical-chemical constants of synthesized monoethers of EG (MEG)

The structure of MEG monoethers	$T_{boil.}$ ^{0}C/20 mm.Hg	d_4^{20}	n_D^{20}	Purity on GLC, %
HCOO-CH_2-CH_2-OH	6.6-6.8	1.1112	1.4197	99.1
CH_3-COO-CH_2-CH_2-OH	85-86	1.1085	1.4208	98.9
CH_3-CH_2-COO-CH_2-CH_2-OH	101-103	1.0050	1.4220	99.0
CH_3-CH_2-CH_2-COO-CH_2-CH_2-OH	110-113	0.9985	1.4258	98.7

At the second stage we have studied the reaction of etherification of synthesized 2-hydroxyethyl ethers of saturated acids in presence of catalyst-ion-exchange acid KU-2-8 of H-form according to the scheme:



R=H; CH_3; CH_3CH_2; $CH_3CH_2CH_2$;

The reactions of obtaining diesters of saturated and acrylic acids were conducted in presence of catalyst of 5%, calculated on the amount of the taken AA. The obtained results are shown in the table 4. To the reaction for preventing of oligomerization of initial AA and obtained acrylates was added hydroquinone of 0.1% mass to AA.

The degree of purity of synthesized diesters was determined by chromatography analyses that are of 97.5-99.0%. In such purity degree was studied physical-chemical constants of synthesized diesters that is shown in table 5.

In order to simplify the obtaining process technology of stated mixed diesters of saturated and acrylic acids, without separation of catalyst KU-2-8 of H-form and benzene solvent from the system and without fractionation of SA monoether from catalysate we added to the reaction mass of 0.1% of hydroquinone and AA continuing the etherification for obtaining MDE. The obtained results were shown in table. 6.

Table 4. Obtaining of mixed diesters of ethyleneglycol (benzene of 100 g., temperature of 80-85^{0}C, time 4 h)

Taken for reaction		Cat. KU-2-8 H, g	Obtained	
HOEFA, g	AA,g		Structure with DE	Yield, %
HCOO-CH_2-CH_2-OH 90	72.0	3.6	$HCOO(CH_2)_2OOCCH_2$=CH_2	92.1

Cont.table4.

CH_3-COO-CH_2-CH_2-OH 104	72.0	3.6	$CH_3COO(CH_2)_2OOCCH=CH_2$	91.5
CH_3-CH_2-COO-CH_2-CH_2-OH 118	72.0	3.6	$CH_3CH_2COO(CH_2)_2OOCCH=CH_2$	90.6
CH_3-CH_2-CH_2-COO-CH_2-CH_2-OH 132	72.0	3.6	$CH_3CH_2CH_2COO(CH_2)_2OOCCH=CH_2$	90.1

Table 5. The physical-chemical constants of synthesized mixed diesters of ethyleneglycol

Structure of diesters	$T_{boil.}$ ^{0}C/ 5 mm.Hg	d_4^{20}	n_D^{20}	The purity degree, DEG
$HCOO(CH_2)_2OOCCH_2=CH_2$	88-89	1.1566	1.4208	98.3
$CH_3COO(CH_2)_2OOCCH=CH_2$	103-105	1.1418	1.4288	99.0
$CH_3CH_2COO(CH_2)_2OOCCH=CH_2$	117-118	1.0873	1.4295	97.5
$CH_3CH_2CH_2COO(CH_2)_2OOCCH=CH_2$	131-133	1.0615	1.4302	98.0

As seen from obtained data shown in Table 6, the yield of mixed diesters by simplified way compiles 88.7-94.5%. Their physical-chemical constants agreed with mentioned in table 5, obtained in two stages.

Table 6. Obtaining of MDE of saturated and acrylic acids EG

Taken for reaction, g.				Cat.	Obtained	
SA	EG	AA	benzene	КУ-2-8 H	structure	%
62.0	FA-46.0	72.0	100.0	3.6	$HCOO(CH_2)_2OOCCH_2=CH_2$	94.5
62.0	AA-60.0	72.0	100.0	3.6	$CH_3COO(CH_2)_2OOCCH=CH_2$	93.9
62.0	PA-74.0	72.0	100.0	3.6	$CH_3CH_2COO(CH_2)_2OOCCH=CH_2$	89.8
62.0	NBA-88.0	72.0	100.0	3.6	$CH_3CH_2CH_2COO(CH_2)_2OOCCH=CH_2$	88.7

The structures of synthesized monoethers of ethyleneglycol of saturated acids and mixed diesters were determined by IR- and NMR $^{'}$H, ^{13}C spectral methods of analysis. In IR- spectrum appears following absorption lines, proving in molecule HOEFA (γ-sm^{-1}), HO-3436.8; 1075.63; CH, CH_2-2835.53; 2982.03; CH_3 1379.17; C=O 1733.15; C-O-C 1177.27; 1276.47.

In IR-spectrum of mixed diesters appears absorption lines in the range of 810 sm^{-1} and 890 sm^{-1} confirming CH_2=CH- groups. However, in spectra are absent the absorption lines of OH-group in molecule of mixed diesters.

In NMR ^1H chem. shift. ethylene group appears in the range of 3.6-4.3 m.d. in the form of singlet and doublet. In acrylate chem. shiftings of CH_2=CH-group appear in the field (range) of 6.25-6.65 m.d. in the triplet form.

IR-spectra were recorded on a spectrophotometer «Bruker», manufactured by ALPA IR-Fure.

NMR ^1H and ^{13}C spectra were recorded on a spectrophotometer «Bruker AV-300» as a solvent acetone- d_6.

The composition and the degree of purity of synthesized, as well as initial compounds were defined by GLC analysis. As adsorbent was applied polyethyleneglycol succinate in the amount of 10 % mass sphere-chrome. The length of column is 1.5m, gas carrier is helium, its rate of 45 ml/min.

The tests for synthesis of mono- and diesters of ethyleneglycol were conducted in equipment Din-Stark.

The initial compounds up to experiments were distilled and they had the following physical-chemical constants:

FA- b.p. . 100.5 ^{0}C; d_4^{20} 1.2205; n_D^{20} 1.3716;

AA- b.p. 118.0 ^{0}C; d_4^{20} 1.0491; n_D^{20} 1.3678;

PA- b.p. 141-141.5 ^{0}C; d_4^{20} 0.9921; n_D^{20} 1.3876;

NBA- b.p. 163 ^{0}C; d_4^{20} 0.9594; n_D^{20} 1.3992;

AA- b.p. 141 ^{0}C; d_4^{20} 0.0601; n_D^{20} 1.4226;

EG- . b.p. 197.0 ^{0}C; d_4^{20} 1.1138; n_D^{20} 1.4316.

The above mentioned physical-chemical constants of the initial compounds agreed with references [7].

Catalyst KU-2-8 for converting to H-form primarily were treated by concentrated hydrochloric acid, washed out with distilled water, dried in thermostat at temperature of 60-70^{0}C.

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