47% aqueous HI, and 0.9 g (0.05 moles) of water. The reaction products were analyzed by means of GLC on a LKhM-8 MD chromatograph with a steel column (l = 2.75 m, d = 3 mm) filled with 15% polyethylene glycol adipate with 3% H₃PO₄ on a Chromosorb Y (60-80 mesh) support at a temperature of 175°C. The temperature for sample introduction was 250°C. A flame ionization detector was used and the rate of carrier gas (helium) was 30 ml/min.

CONCLUSIONS

Palladium complexes of the general formula $PdCl_2L_2$ (L = tri(thienyl)phosphine) are active and selectively reacting catalysts in the carbonylation of C_2-C_{18} α -olefins.

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ESTERIFICATION OF ACRYLIC AND METHACRYLIC ACIDS

WITH OLEFIN OXIDES CATALYZED BY NITROXYL RADICALS

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Acrylates and methacrylates are widely used in the synthesis of thermoplastics and polymers with a three-dimensional reticular structure [1]. In this work a method was developed for obtaining acrylates and methacrylates of the general formula

 $\begin{array}{c}
 0 \\
 CH_2 = C - C - OCH_2CHOH \\
 \| & | \\
 R^1 = H, Me; R^2 = (CH_2)_nH, n = 0 - 8
\end{array}$ (1)

RESULTS AND DISCUSSION

Compounds of type (I) with $R^2 = H$, Me, Et, and n-Bu are obtained by condensation of acrylic or methacrylic acids with ethylene or propylene oxides and epichlorohydrin at temperatures from 80 to 100°C and under pressure from 0.1 to 1.0 MPa in the presence of acidic (anhydrous salts of trivalent Fe and Cr) [2] or basic (C_5H_5N , Et_3N) catalysts [3]. In order to prevent polymerization of acrylic acids and oxyalkyl esters (I) inhibitors {hydro-quinone, its monomethacrylic ester, di(β -naphthyl)-p-phenylenediamine, phenothiazine, methoxy-phenols, and others} are added to the reaction mixture in the amount of 0.01-1.0% based on the amount of acid. Esterification in the presence of these catalysts proceeds with poor selectivity (with formation of up to 5% by-products - diesters, glycols, and oligomers). The mentioned inhibitors are not very effective under the conditions of esterification, particularly at 100°C.

We established [4, 5] the possibility of esterification of acrylic and methacrylic acids by oxides of higher α -olefins with the use of new catalysts - cyclic and acyclic nitroxyl mono- or polyradicals, the properties and synthesis of which are described in [6]. The essential advantage of these catalysts is their highly effective inhibitory properties during polymerization.

Branch of Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Vol. 23, No. 10, pp. 2249-2252, October, 1987. Original article submitted March 10, 1986. TABLE 1. Conditions and Results of Esterification of Acrylic (AA) and Methacrylic (MAA) Acids with Olefin Oxides (OO) Catalyzed by Nitroxyl Radicals {Catalysts: 2,2,6,6-tetramethyl-4-benzoyloxypiperidine-1-oxyl (II), 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (III), bis-2,2,6,6-tetramethyl-4-hydroxy-1-oxylpiperidyl ester of phthalic acid (IV), tetrakis-2,2,6,6-tetramethyl-4-hydroxy-1-oxylpiperidyl ester of orthosilicic acid (V)

Acid	Olefin oxide (OO)	Acid:OO, moles	Catal	[<u> </u>	
			index	concentra- tion, mole % based on acid	Т, °С	Time, h	Acid conver- sion, %	Yield of ester, %
MAA MEE AA MEE AA AA MEE MEE	Ethylene Propylene Butene-1 Hexene-1 Octene-1 Decene-1 Octene-1 Octene-1	$1 : 1,3 \\ 1 : 1,1 \\ 1 : 1,2 \\ 1 : 1,2 \\ 1 : 1,2 \\ 1 : 1,1 \\ 1 : 1,1 \\ 1 : 1,4 \\ 1 : 1,1 \\ 1 : 1 : 1 \\ 1 : 1 : 1 : 1 \\ 1 : 1 : 1 : 1 \\ 1 : 1 : 1 : 1 : 1 \\ 1 : 1 : 1 : 1 : 1 : 1 \\ 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 \\ 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1 :$	(II) (III) (IV) (V) (III) (III) (III) (III)	$0,5 \\ 1,5 \\ 6,0 \\ 4,2 \\ 2,9 \\ 4,0 \\ 0$	100 110 120 120 130 140 80 130	4 5 6 8 18 10	97,2 96,0 96,0 98,0 97,0 97,0 80,0 0	95,0 92,5 94,0 95,2 95,0 94,0 77,0 0

TABLE 2. Characteristics of 2-Hydroxyalkyl Esters of Acrylic and Methacrylic Acids

Teter	Found,%		Molecular	Calculated, %		Molecular weight	
Ester	С	н	formula	С	н	found	calcu- lated
2-Hydroxyethyl methacrylate 2-Hydroxypropyl methacrylate 2-Hydroxybutyl methacrylate 2-Hydroxybexyl methacrylate 2-Hydroxyoctyl methacrylate 2-Hydroxydecyl methacrylate 2-Hydroxyoctyl acrylate	55,3 76,3 76,4 78,3 79,1 80,0 77,8	7,8 11,2 12,0 12,1 11,6 11,1 10,6	$\begin{array}{c} C_6O_3H_{10} \\ C_7O_3H_{12} \\ C_8O_3H_{14} \\ C_{10}O_3H_{14} \\ C_{12}O_3H_{22} \\ C_{14}O_3H_{22} \\ C_{14}O_3H_{20} \end{array}$	53,1 75,0 75,9 77,4 78,5 79,3 77,2	7,7 11,1 11,4 11,8 11,2 10,7 10,3	119 138 151 175 208 235 197	$ \begin{array}{r} 130 \\ 144 \\ 158 \\ 186 \\ 214 \\ 242 \\ 202 \\ \end{array} $

TABLE 2 (continued)*

Feter	Bromide con- tent, grams Br/100 g sample		Ester mg KOF sample	content, I/g	Hydroxyl content,%	
Later	found	calcu- lated	found	calcu- lated	found	calcu- lated
	(00.0				10.0	
2-Hydroxyethyl methacrylate	122,8	123	418	430	13,8	13,1
2-Hydroxypropyl methacrylate	111,6	111	376	388	12,2	11,8
2-Hydroxybutyl methacrylate	99.8	101	348	354	11.1	10,7
2-Hydroxyhexyl methacrylate	84.3	86	298	301	9.4	9,1
2-Hydroxyoctyl methacrylate	73.6	74.8	251	261	8.3	8,1
2-Hydroxydecyl methacrylate	65.8	66.0	228	231	7.3	7.0
2-Hydroxyoctyl acrylate	78.4	79.2	269	277	8.8	8,4

*As in Russian original; appears to be unrelated to article - Editor.

Typical conditions of esterification are shown in Table 1 and characteristic products are in Table 2. Optimal yields of desired product (90-92%) with high conversion of acid (96-97%) are achieved with a small excess of olefin oxide at temperatures of 100 to 160°C. At temperatures >160°C in many cases sublimation and partial decomposition of catalyst is observed.

From Figure 1 it is seen that increase of catalyst concentration (2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl) from 0.01 to 0.1 moles/liter holding the other conditions constant is accompanied by an increase of the consumption rate of methacrylic acid during its esterification by decene oxide. At 140°C and at a concentration of the above catalyst of 0.1 moles/liter the reaction is practically complete in 7 h. In spite of the relatively high temperature and high reaction time, there was no observed polymerization of the starting compounds or products in the course of the reaction or under the conditions of separation of the reaction mixture.



Fig. 1. Influence of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl (III) concentration on kinetics of methacrylic acid (MAA) consumption during its esterification with decene-1 oxide (DO) at 140°C. Molar ratio DO:MAA = 1.1:1; concentration of (III), moles/liter: 1) 0.01; 2) 0.05; 3) 0.10.

Fig. 2. Kinetics of MAA consumption during its esterification with DO at 140°C under the action of: 1) 2,2,6,6-tetramethyl-1-hydroxypiperidinium methacrylate; 2) 2,2,6,6-tetramethyl-1-oxopiperidinium chloride; 3) 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl. Catalyst concentration 2% based on MAA; molar ratio DO:MAA = 1.1:1.

The catalytic activity of the nitroxyl radicals can be explained by considering the results of a mechanistic study of the reaction of nitroxyl radicals with Brønsted acids [7]. In accordance with existing ideas protonation of the radical nitroxyl group occurs, followed by dismutation of the resulting highly reactive intermediate with starting radicals to form hydroxylamines and oxoammonium salts

$$\sum_{\substack{N \to 0 + H0 - C - R \neq \dot{N} - 0H \dots \overline{O}COR \\ 0 \\ N \to 0H \dots \overline{O}COR + 0 \neq N \neq 2 \\ N \to 0H + \sum_{\substack{N \to 0 \\ n \neq 0}} \dot{N} = 0 \dots \overline{O}COR$$

Hydroxylamines (>N-OH) are also reversely protonated by acids to give hydroxylammonium salts

$$N = 0H + RCOOH \Rightarrow N$$

H... $\overline{O}COR$

Esterification of acrylic and methacrylic acids with olefin oxides can be described by the equation



Apparently catalysis of the reaction by oxoammonium salts is also realized by the same path



In order to test the proposed mechanism 2,2,6,6-tetramethyl-1-hydroxypiperidinium methacrylate and 2,2,6,6-tetramethyl-1-oxopiperidinium chloride [8] were synthesized, which, according to the above scheme, are active catalysts of esterification of methacrylic acid by decene oxide at 140°C (Fig. 2).

The above compounds have catalytic activity comparable with that of the corresponding nitroxyl radicals. Due to equilibration at the examined stages in the reaction mixture there are always starting nitroxyl radicals present which effectively inhibit polymerization of the initial acids and the reaction products.

EXPERIMENTAL

Acrylic and methacrylic acids were purified and dried by known methods [9, 10]. Olefin oxides were obtained by epoxidation of α -olefins with tert-butyl hydroperoxide in the presence of molybdenyl bisacetylacetonate [11, 12], followed by purification with an efficient distillation column. The constants of the obtained oxides correspond with data of [11-13]. The nitroxyl radicals were synthesized, isolated, and identified according to [6, 14].

Esterification of acrylic and methacrylic acids with olefin oxides was carried out in metal reactors with noncorrosive coating or in glass reactors under isothermal conditions with vigorous stirring of the reaction mixture. Into the reactor acid, catalyst, and olefin oxide were placed and the reaction mixture was rapidly heated to the assigned temperature. The reaction course was followed by the change of acid number measured by titrometry or gas liquid chromatography {column 2 m long, packed with modified (5% SE-30) chromaton, oven temperature 180°C, LKhM-8MD chromatograph}. The obtained hydroxyalkyl esters of the acrylic and methacrylic acids were isolated with a distillation column and identified by the usual methods.

CONCLUSIONS

1. Nitroxyl radicals are effective and selective catalysts of esterification of acrylic and methacrylic acids by olefin oxides and also they are inhibitors of polymerization of the starting materials and final products.

2. A mechanism for the catalytic action of nitroxyl radicals in this reaction is proposed and a series of hydroxyalkyl esters of acrylic acids is obtained.

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