ORGANIC CHEMISTY

TRANSFORMATION OF METAMERIC ESTERS ON NEODYMIUM AND ERBIUM OXIDES

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The transformation of esters can proceed in two directions on heterogeneous catalysts [1]:



1) with the formation of aldehydes, in which connection the same products are obtained from metameric esters, and 2) with the formation of alcohol and ketone (the transformation products of the metameric esters are different).

On Cu catalysts, promoted with ThO_2 , products of similar composition were obtained from the metameric esters and their mixtures [2], which testifies to the predominantly aldehyde direction of their decomposition. On the same catalysts from esters, the possible intermediate ketonization products of primary alcohols, are formed aldehydes at 300-400°C, while ketones are formed mainly at higher temperatures [3]. The authors of [2, 3] postulate that ketonization in this case proceeds via the aldol condensation of the aldehydes that are formed from RCOOR', and that the direct formation of ketones from esters is slight.

The role of esters in the catalytic ketonization of primary alcohols on the oxides of rare-earth elements has not been established [4, 5]. In view of this we studied the transformation of two pairs of metameric esters: n-butyl propionate (BP) and n-propyl butyrate (PB), and isobutyl propionate (IBP) and propyl isobutyrate (PIB), on Nd₂O₃ and Er₂O₃.

EXPERIMENTAL

The catalysts were obtained by heating the Nd and Er hydroxides [6] in the air at 550° C. The starting compounds were synthesized from the alcohols and acids [7], dried over anhydrous MgSO₄, and distilled. Into the reactor was charged either 2 g of Nd₂O₃ or 1.25 g of Er₂O₃, which corresponded to a total surface area of 40 m². The samples, with a granule size of 1-2 mm, were mixed with quartz particles of the same size. The volume of the diluted catalyst was 4 ml.

The experiments were run in a flow system in a stream of dry N_2 at 325-400°, the partial pressure of the ester was 75 torr, and its feed rate was 0.2 mmole/m²·h. To establish the effect of water, which is formed by the parallel crotonic condensation of aldehydes, the experiments were repeated in a stream of moist N_2 (9 mg of $H_2O/liter$). Prior to experiment the catalysts were heated for 1 h in an N_2 stream at 550°. The activity of the samples remained practically constant during experiment and was reproduced after regeneration, which was done by heating at 550° for 5 h in a stream of air, freed of CO₂ using ascarite.

The liquid products were analyzed on an LKhM-8M chromatograph equipped with a katharometer. For the BP and PB catalyzates we used a 3 m \times 3 mm column packed with 10% of 1,2,3tris(2-cyanoethoxy)propane deposited on 50-70 mesh kieselguhr (70°, helium flow rate = 30 ml/min; for separating the butanol and PB, a temperature of 45° and a helium flow rate of 45 ml/min), while for the IBP and PIB catalyzates we used a 1.7 m \times 3 mm columm packed with 15% Carbowax-20M deposited on Chromaton N-AW-DMCS (70°, helium flow rate = 30 ml/min). To separate the ethyl isopropyl and diisopropyl ketones we ran additional analyses on a Chrom-2 chromatograph equipped with a flame-ionization detector (50-m capillary columm packed with 5%

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1828-1833, August, 1980. Original article submitted July 25, 1979. squalane, 90°, and N_2 flow rate = 40 ml/min). Correction factors, which were determined by analyzing mixtures of known composition, were used in the calculations.

DISCUSSION OF RESULTS

As can be seen from Tables 1 and 2, at $325-400^{\circ}$ the main transformation products of the esters are alcohols and ketones. Here Er_2O_3 is much less active than Nd_2O_3 : approximately the same degrees of transformation of the starting esters and yields of the main products were obtained on Er_2O_3 at temperatures that were 25° higher. The catalyzates, obtained on Nd_2O_3 , especially at $375-400^{\circ}$, contain appreciable amounts of aldehydes and their further transformation products. It is possible that the greater activity of Nd_2O_3 when compared with Er_2O_3 in the condensation of aldehydes [5] is one of the reasons for its higher activity in the aldehyde direction of the decomposition of esters.

The transformation of BP and PB leads to different products (Table 1). n-Butanol and diethyl ketone are formed from BP, while n-propanol and dipropyl ketone are formed from PB. The alcohol/ketone mole ratio = 2, which corresponds to the following scheme:

$$2RCOOCH_{2}R' + H_{2}O \rightarrow RCOR + 2R'CH_{2}OH + CO_{2}$$

Propionaldehyde and butyraldehyde, and their further transformation products, namely ethyl propyl ketone, and also dipropyl ketone from BP and diethyl ketone from PB, are formed in small amounts at high temperatures.

The transformation of the other pair of metameric esters also proceeds differently (Table 2). At 375°, isobutanol and diethyl ketone are formed mainly from IBP in a mole ratio of 2:1. Below 375° this ratio increases, while at 400° it decreases. This is possibly due to partial progress of the reaction by the Sabatier scheme [8]:

$2\text{RCOOCH}_2\text{CH}_2\text{R}' \rightarrow \text{RCOR} + \text{R'CH}_2\text{CH}_2\text{OH} + \text{R'CH} = \text{CH}_2 + \text{CO}_2$

Diisopropyl ketone and ethyl isopropyl ketone are formed in small amounts on Nd_2O_3 at 400°. In the transformation of PIB the main products are n-propanol and diisopropyl ketone in a mole ratio of 2:1 on Nd_2O_3 at 400°, while in the other cases it is higher.

Butyl propionate is more reactive than PB: under the same conditions the total conversion of the former and the yields of the main products, namely alcohol and ketone, are considerably higher (Table 1). This can be due to the different reactivity of the possible intermediate products and, in particular, to the faster conversion rate of propionic acid when compared with butyric acid. Actually, propionic acid is ketonized to the extent of 40% on Nd_2O_3 at 305° , and at 340° in the case of butyric acid.

Isobutyl propionate is less reactive than BP (Tables 1 and 2) under the same conditions the total conversion and yields of aldehydes and diethyl ketone are lower. PIB is definitely less reactive than PB. Thus, at 350° on Nd_2O_3 the total conversions of these esters were, respectively, 12.5 and 45.5%. Apparently, the differences appear even in the step of hydrolyzing the esters, since the yield of n-propanol from PIB is considerably lower than from PB (at 375° on Er_2O_3 it is respectively, 3 and 19%). The lower reactivity of the esters that contain a branched alcohol group, and especially a branched acid group, can be due to steric hindrance, both during the decomposition of the esters and during the further transformations of the isoaldehydes and isoacids.

The selectivity of the decomposition of the esters along the ketone and aldehyde directions can be judged by the total yields, when based on converted ester, of alcohol and ketone (S_2) , on the one hand, and of aldehydes and their condensation products (S_1) , on the other hand (see Tables 1 and 2). Thus, at 350° on Er_2O_3 the S_2/S_1 ratio in the case of the transformations of PB is 3.5 higher, while for BP it is 9.5 times higher than on Nd_2O_3 . An increase in the temperature favors the formation and further transformation of the aldehydes and the S_2/S_1 ratio decreases. The yields of aldehydes and their condensation products from PIB on Nd_2O_3 approach the yields of propanol and diisopropyl ketone. The S_2/S_1 ratio in this case is considerably smaller than for the other esters, while at 400° it approaches one.

As a rule, in the presence of water both the total conversion of esters and the yields of the main products increase. The alcohol/ketone ratio usually exceeds 2 and decreases with increase in the temperature. As a rule, the amount of aldehydes in the reaction products when water is added decreases and S_2/S_1 increases. However, the catalyzates obtained from the propionic acid esters contain noticeable amounts of the further condensation products of

			52,7	13,0 9,3	7,6 7,6	395,0		$ 21,6 \\ 16.3 \\$	26.0	11,5	5,7	7,0
\$ ¹			1,8 4,8	4,7 9,7	10,6	14,0 14,0		550 555		6,0	14,0	11,5
S_{2}^{*}			90,0 86,7	60,3 90,3	79,8	84,8 85,5		86,8 90,5 32,0	68,4	78,5	00,9 78,5	
Alcohol : ketone mole ratio			2,0	3,0 2,5	2,0	240 740		2,0 2,0	14 19 19 19	2,0	2,0 2,0	50,
Conversion of ester, ϕ_b	total		28,5 66,0	22,5 32,5	35.5 74 5	46,5 93,5		21,5 47,5 12,5 16,0	25,5	45,5 97 F	44,5 84,5	
	to butyral- dehyde con- densation products		0,5	0,7 2,9	ł	1,3	butyrate			0,4	1,5	0,9
	to di- propyl ketone		11	I I	1	1,0,1		8,0 19,5	1,0	7,7	16,3	28,7
	to ethy l propyl ketone	pionate		11	0.5 0.5	414		0,1	- 1 1	1	1,0	3,8
	to dieth- yl ke- tone	n-Butyl pro	8,0 19,0	3.5 8,5	8,5 9,5 119,0 25,0 25,0 11,5 25,0 0,0 0,9	0.5	0 , 3	5,6 0,6	1,3			
	to- butanol		$\frac{15,0}{32,5}$	8,7 18,0	16,0 30,5	24,0 47,0		111	1	0,7	2,0	
	to pro- panal		- 0,5	1 1	0,2 7,7	2,1		8,8 19,2	000	8,0	15,8 2,5	31,0
	to buty r - alde- hyde		00100 0000 0000 440 00100 0000 1440	0,3	0,2	0,7	0,6					
	to pro- pional- dehyde		0,2	1 1	0 , 4	0,3		0,1		0,5	1,5	2,0
	т., °С		350	325 T 350 T	325	325 + 350 +		350 375	325 + 350 +	325	350	3501
	Catalyst		$\mathrm{Er}_{2}\mathrm{O}_{3}$		Nd_2O_3			Er_2O_3		Nd_2O_3		

TABLE 1. Transformations of n-Butyl Propionate and n-Propyl Butyrate on Neodymium and Erbium Oxides

н. 2 2 based on converted ester.

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TABLE 2. Transformations of Isobutyl Propionate and Propyl Isobutyrate on Neodymium and Erbium Oxides

based on converted ester. $^{\dagger}\mathrm{The}$ experiments were run in the presence of water.

the aldehydes. Thus, at 400° on Nd₂O₃ the yield of isobutyraldehyde from IBP decreases in the presence of water from 14 to 8%, while the yield of ethyl isopropyl ketone simultaneously increases from 2 to 13%. When PIB is decomposed in the presence of water the yield of the catalyzate increases and the total conversion decreases due to a decrease in the yield of diisopropyl ketone and cracking products. The alcohol/ketone ratio in the catalyzate increases noticeably. The ketone is not formed on Er_2O_3 at 375°, and on Nd₂O₃ at 350°.

As a result, in the studied temperature range the esters are transformed on the Nd and Er oxides to give aldehydes, as well as alcohols and ketones, in which connection the latter direction predominates, especially on Er_2O_3 , at low temperatures, and also in the presence of water in the case of the straight-chain esters. In contrast to the results for a Cu catalyst [2], the data obtained by us on rare-earth oxides permit making the postulation that, besides the aldol and ester scheme, primary alcohols can undergo ketonization. In such case the formation of n-butanol from butyraldehyde [5] can be due to the decomposition of butyl butyrate. It was shown by special experiments that butyral is not hydrogenated under these conditions. The absence of noticeable amounts of butyl butyrate in the transformation products of butanol [4] and butyraldehyde [5] can be due to its greater tendency to decompose when compared with desorption in the gas phase.

CONCLUSIONS

Esters are transformed on the neodymium and erbium oxides to give aldehydes, as well as alcohols and ketones, in which connection the latter direction predominates. Transformation products that differ in composition are formed from the metameric esters. Neodymium oxide is much more active than erbium oxide.

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REACTION OF 3-SULFOLENE WITH 1,3-DIENES, CATALYZED BY PALLADIUM COMPLEXES

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It was recently shown by us that a mixture of the cis-trans-2,5-divinylsulfolanes (I) can be obtained by the reaction of 3-sulfolenes with butadiene in the presence of complex Pd-containing catalysts [1, 2]:



To expand the utility range of the given method for obtaining the (I) derivatives, and also to study the effect of the structure of the 1,3-diene on the direction and structural selectivity of the indicated reaction, we studied the reaction of 3-sulfolene with isoprene, trans-piperylene, 1-acetoxy-1,3-butadiene (AB), and the methyl ester of butadiene-1-carboxy-

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