OXIDATIVE DEHYDROGENATION OF n-HEXANE IN PRESENCE OF HYDROCHLORIC ACID

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The oxidative dehydrogenation of n-hexane with iodine leads mainly to dehydrocyclization with the formation of benzene in up to 52% yield, while the amount of hexenes is less than 1% [1, 2]. It was shown by us [3] that on iron oxide, deposited on KCl-containing silica gel, in the presence of hydrochloric acid and air, the products formed from n-hexane are mainly hexenes, while the yield of benzene is insignificant.

In the present paper we studied the oxidative dehydrogenation of n-hexane on a CsCl-containing iron oxide catalyst [4] in the presence of hydrochloric acid as a function of the temperature, feed rate, and ratio of reactants. In addition, the dehydrochlorination of 1-chlorohexane (CH) on the same catalyst was studied in a stream of air.

EXPERIMENTAL METHOD

The method used to prepare the catalyst (12% Fe_2O_3, 5% CsCl, 83% SiO_2, granule size 2-3 mm) was described in [4]. The experiments were run in flow equipment, equipped with a vertical furnace, in a quartz reactor (i.d. 8 mm), into which was charged either 2 or 4 ml of the catalyst. The hexane feed rate was changed by changing the amount of catalyst. The empty space in the tube was filled with broken quartz. Each experiment lasted 2 h, after which the catalyst was heated in an air stream at 580°. The n-hexane and 25% HCl solution were fed from injector burets, while the air was supplied from a cylinder through a fine control valve. The catalyzate was collected in a coil receiver, cooled in a mixture of ice and salt. The hydrocarbon layer was separated, washed free of HCl, dried, and weighed. The composition of the liquid reaction products was determined on a KhL-4 chromatograph.

1-Chlorohexane (bp 135.0° (760 mm), n_D^{20} 1.4200) was obtained by the treatment of hexyl alcohol with $SOCl_2$ [5]. The experiments with CH were run in either an air or nitrogen stream at 400°; the CH was fed from an injector buret at a space velocity (SV) of 1 h^{-1}, the nitrogen was supplied from a gas meter, while the air was supplied from a cylinder.

DISCUSSION OF RESULTS

With increase in the reaction temperature from 474 to 562°, but at a constant mole ratio of the components, $C_6:O_2:HCl = 1:0.7:1.1$, and a SV in hexane of 1 h^{-1}, the catalyzate yield and the hexane conversion showed little change, and on the average were, respectively, 68.5 and 56.2% (Table 1). The yield of the principal reaction product, namely hexenes, varies as a function of the temperature and has a weakly expressed maximum at 515°. With increase in the reaction temperature from 474 to 515° the yield of hexenes increases from 16.8 up to 23.3% (based on hexane passed through), while with further increase in the temperature up to 562° the yield drops to 12.8%. The yield of the other products hardly changes with change in the temperature, and is equal to 3.5% for benzene, 4.5% for the hexadienes, and 5% for the cracking products.

A study of the effect of the ratio of the components and the space velocity was run at 520°, where the yield of the olefins was highest (Figs. 1 and 2). With a constant hexane feed rate, the relative amount of O_2 or HCl was varied. At a hexane SV of 1 h^{-1} and a $C_6:HCl$ ratio = 1 : 2.0 the yield of hexenes, as a function of the relative amount of O_2 in the mixture, reaches its highest value (~20%) at a $C_6:O_2$ ratio = 1 : 0.7.

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TABLE 1. Effect of Temperature on Oxidative Dehydrogenation of Hexane ($C_6H_{14} : O_2 : HCl = 1 : 0.7 : 1.2$; SV of Hexane = 1 h^{-1})

T., °C	Catalyzate yield, %	C_6H_{14} conversion, %	Yield when based on hexane passed through, %			
			cracking products	hexenes	hexadienes	benzene
454	67,2	52,1	0,3	16,8	1,8	0,5
504	72,0	47,9	0,6	16,5	2,0	0,8
515	68,3	60,6	0,5	23,3	3,5	1,4
521	72,4	58,8	1,5	22,6	4,5	2,5
527	69,8	57,9	2,2	20,5	3,9	1,0
544	67,0	58,2	5,4	15,4	2,8	1,6
562	62,5	57,7	1,1	12,8	2,8	3,4

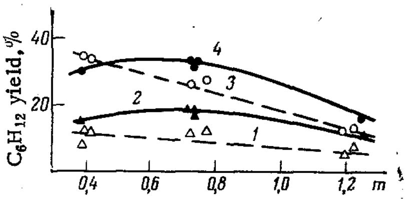

Fig. 1

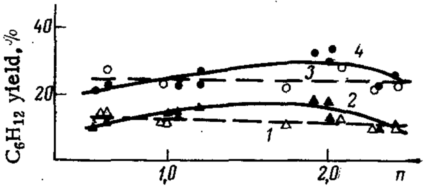

Fig. 2

Fig. 1. Yield of hexenes as a function of amount of oxygen in mixture $C_6H_{14} : O_2 : HCl = 1 : m : 2$. Yield (%) when based on hexane passed through at a SV of 2 h^{-1} (1) and 1 h^{-1} (2), and when based on reacted hexane at a SV of 2 h^{-1} (3) and 1 h^{-1} (4).

Fig. 2. Yield of hexenes as a function of amount of HCl in mixture $C_6H_{14} : O_2 : HCl = 1 : 0.7 : n$. The designations are the same as in Fig. 1.

With a twofold increase in the hexane feed rate the yield of hexenes is inversely proportional to the relative amount of O_2 in the mixture, and changes from 13 to 6% when the amount of O_2 is changed from 0.4 to 1.2 moles/mole of hydrocarbon (see Fig. 1). In Fig. 2 is shown the effect of the relative amount of HCl in the mixture on the yield of hexenes at a constant $C_6 : O_2$ ratio = 1 : 0.7. The yield of hexene is highest (~20% when based on hexane passed through) at a hexane SV of 1 h^{-1} and 2 moles of HCl/mole of hydrocarbon. When the hexane space velocity is increased up to 2 h^{-1} the yield of hexenes decreases to 14-12%, and is practically independent of the amount of acid in the mixture.

From the obtained data it can be seen that the highest yield of hexenes is obtained in the range 515-520° at a hexane SV of 1 h^{-1} and a molal ratio of the components of $C : O_2 : HCl = 1 : 0.7 : 2.0$. All of the isomeric n-hexenes are obtained independent of the reaction conditions, in which connection the yield of 1-hexene is 23% (of the total amount of hexenes), that of the 2-hexenes is 32%, and that of the 3-hexenes is 45%. This ratio of the isomers is strongly different from the equilibrium ratio. Isomerization of the hydrocarbon skeleton is practically nonexistent: the amount of isohexanes is less than 1%. Oxygen-containing compounds were not detected.

Employing elemental analysis and GLC, CH was detected in the catalyzate (10% of the catalyzate). It was shown that CH can be converted to hexenes on an iron oxide catalyst at high temperature in either a nitrogen or an air stream: CH in nitrogen at 400° and a chloride SV of 1 h^{-1} was converted to the extent of 57% to hexenes (Table 2), while in an air stream at the same temperature the yield of hexenes is only 31% due to marked tarring of the products. Of the other possible reaction products only hexadienes (~1%) were found. The absence of benzene in the reaction products can be explained by the low reaction temperature. It is interesting that the relative amounts of n-hexene isomers, obtained from CH in an air stream (respectively 21, 34, and 45% for 1-hexene, 2-hexene, and 3-hexene), are nearly the same as in the oxidative dehydrogenation of n-hexane. It is probable that the formation of all three n-hexene isomers from CH is not associated with their isomerization into each other, since then their ratio would be close to the equilibrium ratio, but rather with the conditions of HCl cleavage and addition. Apparently, both in the case of n-hexane and CH, the hexenes are formed via the same activated complex.

The presence of CH in the catalyzate and the conversion of CH to hexenes both serve to corroborate the previously expressed theory that successive chlorination of the hydrocarbon and dehydrochlorination of the alkyl chloride occurs during the oxidative dehydrogenation of paraffin hydrocarbons with hydrochloric acid [6].

TABLE 2. Yields of Reaction Products of 1-Chlorohexane (CH) on Iron Oxide Catalyst (400°, SV = 1 h^{-1})

Starting mixture, moles	Catalyzate yield,%	Yield when based on CH passed through,%			
		cracking products	hexenes	hexadienes	benzene
CH : N$_2$ = 1 : 3,8	64	0	57,1	1,1	0
CH : O$_2$ = 1 : 0,7	45	0,2	30,6	0,7	0

CONCLUSIONS

1. Under the optimum conditions the main direction of the oxidative dehydrogenation of n-hexane in the presence of hydrochloric acid and iron oxide, deposited on silica gel containing CsCl, is the formation of n-hexenes, the yield of which reaches 22-23% when based on hexane passed through, or 38% when based on reacted hexane.

2. n-Hexenes, with the same ratio of the isomers as in the oxidative dehydrogenation of n-hexane with hydrochloric acid, are formed from 1-chlorohexane on the same catalyst in an air stream, at 400°, and a chloride space velocity of 1 h^{-1}.

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