Reactions of normal alcohols in the presence of a dehydrogenating iron catalyst

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The oxidizing condensation of normal alcohols C_4 to C_{12} in the gas phase over Fe_3O_4 catalyst containing Cr, Si and K oxides was studied. The reactions were carried out in a continuous process at atmospheric pressure. Initially the alcohols undergo dehydrogenation to aldehydes and esters, and at higher temperatures symmetric ketones containing $2n-1$ atoms of carbon in a molecule are formed. A mechanism for the reaction is proposed.

Keywords: ketonization, iron catalyst, β-hydride transfer

Alkylating hydroxyarenes with normal alcohols over an iron catalyst [1–3] we have recently found that as the molecular weight of the alcohol increases, the selectivity of the alkylation decreases. In fact, beginning with n-butanol the alcohols undergo to higher and higher degree concurrent reactions turning into aldehydes and undergo condensation, forming esters and at higher temperatures ketones.

Formerly the ketonization of higher alcohols was carried out in the presence of catalysts containing copper, bronze alloys, chromium and zinc oxide, or a combination of copper with chromium, e.g., copper chromites [4–6].

The purpose of this study was to examine the properties of an iron catalyst in reactions of normal alcohols, and if possible to show that it provides a convenient method for the synthesis of higher aliphatic ketones that may find wide application, as well as become a material in further syntheses, e.g., in the production of a new generation of highly effective double fail surfactants [7,8]. An improvement of the effectiveness of surfactants creates a real possibility of relieving the environment. The oxidizing condensation reaction also meets the requirements for modern technological solutions in the sense of the principle discussed by Sheldon [9,10] to maximize the number of atoms passing from the reactant to the product. It is also environment-friendly, as no noxious by-products are formed, and it could become a method befitting the trends in the chemical industry [11].

The catalyst, containing Fe, Si, Cr and K oxides in the molar ratio of 100 : 2 : 1 : 0.1, was obtained from a solution containing a mixture of iron and chromium nitrates, as well as sodium silicate, by coprecipitation with an aqueous solution of ammonia (1 : 1) at room temperature until pH 7 was reached. The suspension obtained was washed out several times with distilled water until nitrate ions are removed and filtered. The precipitate was dried, pelleted with 3 wt% addition of graphite and calcined at 743 K for 5 h. The crushed pellets were impregnated with a water solution of potassium carbonate, dried and calcined again at 743 K/5 h. The fresh catalyst is γ-Fe_2O_3 with a specific surface area, S_{BET}, of around 60 m^2/g, upon reduction it transforms into Fe_3O_4 of S_{BET} of around 40 m^2/g and the pore volume V_{p}(0–50 nm) equal to 0.23 cm^3/g. More specific information on the physico-chemical properties of this catalyst is contained in [1].

The ketonization reaction of the normal alcohols was carried out in a standard flow system, under atmospheric pressure in the gas phase. A vertical quartz reactor of 8 mm inner diameter filled with the catalyst of a granularity of 0.6–1.2 mm was used. The raw material – a normal aliphatic alcohol – was fed in a continuous manner from the reactor's top using a micropump. The catalyst was pre-reduced with methanol at 473 K for 1 h, then the substrate was fed. Experiments were carried out as a function of increasing temperature, where at pre-chosen temperatures, after the stationary equilibrium had set in, the proper experiments were carried out for ca. 2 h. After a series of experiments, the catalyst was regenerated with air at 743 K. The condensed products of reaction were analyzed by gas chromatography and mass spectroscopy. The gas chromatograph HP 6890 was provided with a FID detector and a capillary column HP-5 (30 m × 0.32 mm filled with phenyl methyl silicone). Products were identified by mass spectroscopy (HP MSD 59). The gaseous products were examined in respect of the content of carbon oxide, carbon dioxide and hydrogen.

Table 1 presents the dependence of the conversion of n-decanol on temperature and the yield of the main products in the experiments carried out at the load of 1.0 h^{-1}.

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Table 1
The results of n-decanol condensation over iron catalyst; load 1.0 h^{-1}.

Reaction temp. (K)	Conversion (%)	Yield of reaction products (%)				
		n-decane	n-decanal	decyl decylate	10-nonyldecanone	other
573	17.0	1.5	2.9	6.9	0	0.3
593	33.4	1.8	4.8	19.5	0	0.3
608	46.1	2.6	7.5	21.9	1.5	0.4
625	64.0	6.7	9.0	15.0	15.0	0.9
633	75.0	7.6	6.3	8.0	31.2	1.9
643	97.9	14.3	0	0.6	49.4	8.8
653	99.0	17.3	0	0	42.0	11.7

Table 2
The results of n-decanol condensation over iron catalyst; load 3.0 h^{-1}.

Reaction temp. (K)	Conversion (%)	Yield of reaction products (%)				
		n-decane	n-decanal	decyl decylate	10-nonyldecanone	other
578	18.9	2.3	2.7	9.5	0	0.4
595	28.9	3.8	4.5	13.6	0	0.1
611	39.9	5.2	6.1	19.4	1.1	0.1
628	54.9	7.6	7.7	21.1	4.9	1.1
645	81.8	10.9	6.9	18.7	23.4	2.3
655	98.8	12.2	0.9	0.8	55.8	5.9
665	99.1	12.7	0	0	55.0	5.6

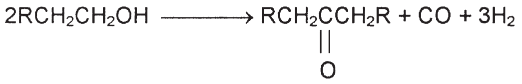
Table 3
Yields of symmetric ketones received in condensation reactions of alcohols n-C_4 to n-C_{12} over iron catalyst; load 1.0 h^{-1}.

Reaction temp. (K)	Yields of ketones received from normal alcohols n-C_4 to n-C_{12} (%)				
	Alcohols				
	n-C_4	n-C_6	n-C_8	n-C_{10}	n-C_{12}
598	0.5	0.5	–	1.5	1.5
618	4.0	5.5	1.0	8.0	7.0
625	4.1	8.0	10.0	15.0	17.5
633	7.5	16.5	25.0	31.0	33.0
640	10.0	24.0	36.0	44.5	48.0
643	18.0	27.5	41.0	49.0	45.0
653	28.0	42.0	47.0	42.0	
660	36.0	45.0	44.0		
668	42.0	38.0			
682	33.0				

The results of condensation of n-decanol at a higher load, equal to 3.0 h^{-1}, are presented in table 2. In this case a higher yield of the ketone (10-nonyldecanone) was obtained, which indicates a possibility to improve results by an appropriate choice of reaction parameters.

In table 3, the results of condensation of normal aliphatic alcohols n-C_4 to n-C_{12} are presented. As the length of the carbon chain of the alcohol increases, the yield of the resulting ketones increases too, with their maximal yield being obtained at lower and lower temperatures.

The reaction of transformation of alcohols into ketones in the presence of an iron catalyst proceeds in accordance with the summary equation:



$$2RCH_2CH_2OH \longrightarrow RCH_2\underset{\underset{\textstyle O}{\|}}{C}CH_2R + CO + 3H_2 \qquad (1)$$

This reaction can only be carried out on a solid catalyst: a similar reaction in solution, i.e., a homogeneous phase, is not known. Condensation of two molecules of alcohol with the formation of a ketone implies a dramatic structural change, and such a reaction has to proceed through several intermediate stages. It can be seen from tables 1 and 2 that at lower temperatures, there are an aldehyde (n-decanal) and an ester (decyl decylate) in the reaction mixture, with the dominance of the latter. It is only at higher temperatures that the ketone appears, at the expense of the aldehyde and ester. At high temperatures (653–673 K), the aldehyde and ester disappear, and the ketone is formed with maximum yield. Hence a conclusion imposes itself that the aldehyde and then the ester are intermediate products of reaction (1). We verified this conclusion ketonizing n-decanal and decyl decylate. In both cases 10-nonylodecanone was a product of the reaction. For this reason we are able to propose the main stages of reaction (1).

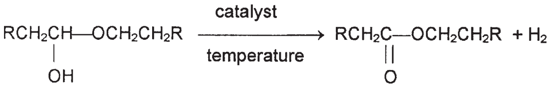
The alcohols undergo adsorption on the oxide catalyst in the form of alkoxides, a proton is detached from the OH group of the alcohol, which is bound by the oxygen from the iron oxide. At higher temperatures, the alkoxy anion loses a hydrogen atom in the form of a hydride anion from the β position in relation to the Fe atom (β-hydride transfer). The hydride anion binds itself indirectly with the iron atom, and then with the proton detached from the OH group of the alcohol, yielding a hydrogen molecule (H_2). As a result we have the reaction of dehydrogenation of an alcohol to an aldehyde:

$$RCH_2CH_2OH \xrightarrow[\text{temperature}]{\text{catalyst}} RCH_2CHO + H_2 \qquad (2)$$

The aldehyde formed in reaction (2) reacts in a non-catalytic process with the alcohol to give a hemiacetal:

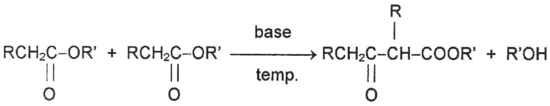
$$RCH_2CHO + RCH_2CH_2OH \rightleftharpoons RCH_2\underset{\text{OH}}{\underset{|}{CH}}—OCH_2CH_2R \qquad (3)$$

Reaction (3) proceeds with great ease: it suffices for example to mix n-decanol with n-decanal and the respective hemiacetal, which is a crystalline compound, is formed with quantitative yield. Hemiacetals are alcohols and will be adsorbed on an iron catalyst in the same way as normal alcohols are. They will, however, undergo dehydrogenation more easily than common alcohols, because they have a strongly electron-donating alkoxy substituent at the α carbon (in relation to the oxygen). Thus, there occurs another reaction, similar to reaction (2):



$$RCH_2\underset{\text{OH}}{\underset{|}{CH}}—OCH_2CH_2R \xrightarrow[\text{temperature}]{\text{catalyst}} RCH_2\underset{\text{O}}{\underset{||}{C}}—OCH_2CH_2R + H_2 \qquad (4)$$

As a result of reaction (4) an ester is formed. Recently, when exploring the mechanism of the Tishchenko reaction, the authors [12] have postulated: hemiacetal bound to lanthanoid metal as key intermediate, which upon hydride transfer to metal gave an ester. It is known that under influence of strong bases, esters of aliphatic carboxylic acids undergo the Claisen and Dieckmann ester condensation [13]. The catalyst we used has basic character and it should be presumed that the similar reaction occurs on its surface at higher temperature:

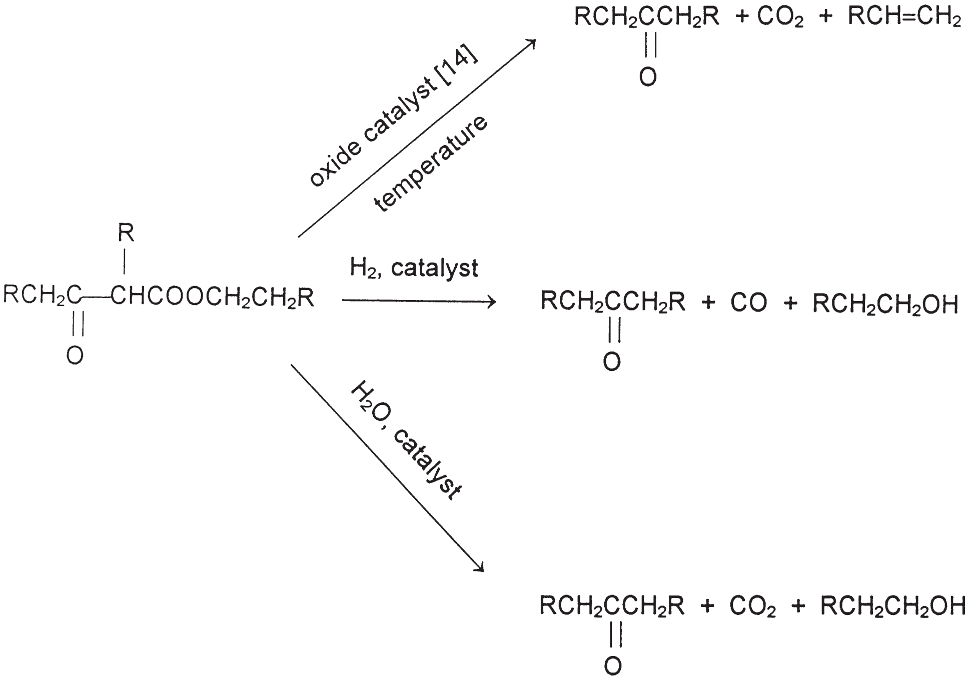


$$RCH_2\underset{\text{O}}{\underset{||}{C}}\text{-}OR' + RCH_2\underset{\text{O}}{\underset{||}{C}}\text{-}OR' \xrightarrow[\text{temp.}]{\text{base}} RCH_2\underset{\text{O}}{\underset{||}{C}}\text{-}\overset{\text{R}}{\overset{|}{C}}H\text{-}COOR' + R'OH \qquad (5)$$

Under the conditions of the process, the β-ketoester formed as a result of reaction (5) is an unstable compound. It might break down through several paths into the desired ketone and several by-products, according to scheme 1.

It is difficult to propose at present a more detailed mechanism of the ester condensation on basic oxide catalysts, as this process has only been studied little so far. Interesting, though at the same time difficult to explain, is the fact that the efficiency of the condensation of alcohols to ketones increases with the increase of their molecular weight.

During the ketonization of the alcohols no resin or tar type deposits were observed on the catalyst. The resulting



Scheme 1.

ketones of higher molecular weight (above C_{15}) are solid substances that may easily be purified by crystallization from n-hexane.

Condensation of higher alcohols in the presence of an iron catalyst makes it possible to produce ketones with a good yield. From technological and environmental standpoint, this is a proposal that meets modern process requirements. The theoretical yield of the reaction is high because of a loss of only one carbon atom in the reaction equation. The atom saving rate improves as the length of the alkyl chain increases. The reaction of condensation of alcohols to ketones is highly interesting also from the standpoint of knowledge and its study is being continued.

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