EFFECTIVE GAS-PHASE DEOXYGENATION OF ALCOHOLS
AND KETONES ON IRON CATALYST

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Abstract: A method of gas-phase deoxygenation of alcohols and ketones into hydrocarbons on iron catalyst at 600 K and $1-2 \cdot 10^5$ Pa is discussed.

In organic chemistry, hydrodeoxygenation of alcohols and ketones into hydrocarbons is widely used as a synthetic as well as structural-analytical method. Despite the availability of quite effective methods for carrying out such reactions in solution, much interest is still being shown in new methods of deoxygenation. One of the latest trends of investigations made in this field is the finding of effective reactions, particularly gas-phase react- ions,[1] which will proceed in the presence of heterogeneous catalysts.[1,2] Our interest to gas-phase deoxygenation is conditioned not only by its synthetic possibilities, but also by the need for pre- and post-column derivatization in the inlet system of gas chromatograph/mass spectrometer in ascertaining the carbon-skeleton structure of alcohols and ketones. The latter application of gas-phase deoxygenation places several requirements on the reactions in- volved: (a) these reactions should be fast, selective, and nearly quantita- tive; (b) the reactions should proceed at pressures usually maintained in a gas chromatograph ($\sim 1-3 \cdot 10^5$ Pa).

According to the available literature data, gas-phase deoxygenation of alcohols or ketones can be carried out in the presence of a Ni,[1-4] WS_2, MoS_2,[4,5] Cu-Cr,[4] Pt or Pd[4] catalyst. These catalysts, however, proved to be unfit for our studies, because they ensure quantitative yield of hydrocarbons only at high partial pressures of hydrogen, as a rule. Hydrodeoxygenation may be as- sumed to proceed quite effectively on a fused iron catalyst because it is active both in hydrogenation and dehydrogenation processes.[6-9] That is why we studied the possibility of using this catalyst for gas-phase deoxygenation of alcohols and some ketones, with the type of carbon skeleton being kept intact.

Reaction was accomplished in a stainless steel microreactor connected to the chromatographic column of a gas chromatograph/mass spectrometer LKB-2091. Hydrogen used as reagent and carrier gas was admitted into the system at a rate of 10-30 ml/min. The catalyst comprising fused iron promoted by V_2O_5 was prepared by a usual technique;[7] 0.1-0.3 g of catalyst in the form of grains

(1-3 mm diameter) was used. Prior to investigation, the catalyst was reduced with hydrogen at 720 K for 2 h. The structure of hydrocarbons formed was ascertained mass spectrometrically.

At 600 K and pressure $1-3 \cdot 10^5$ Pa in the catalysis zone the investigated alcohols and ketones (taken in amounts of 0.1-0.5 μl) were found to undergo quantitative hydrodeoxygenation into corresponding hydrocarbons (see Table 1) in nearly quantitative yield. Despite the fact that conversion takes place at a comparatively high temperature, no destruction of substrates was detected and all the hydrocarbons retained the carbon skeleton of alcohols or ketones.

Table 1. Gas-phase hydroxygenation of alcohols and ketones on an iron catalyst (T = 600 K; P_{H_2} = $1.5 \cdot 10^5$ Pa; H_2 to substrate ratio = 100)

Substrate	Hydrocarbon[*]	Integral rate, $\dfrac{m\ mole}{g\ cat.\ min}$
1	2	3
Aliphatic alcohols		
Primary		
n-Butanol	n-Butane	1.1
iso-Butanol	iso-Butane	1.0
n-Hexan-1-ol	n-Hexane	0.8
n-Octan-1-ol	n-Octane	0.6
2-Ethylhexan-1-ol	3-Methylheptane	0.6
n-Nonan-1-ol	n-Nonane	0.6
n-Decan-1-ol	n-Decane	0.5
n-Undecan-1-ol	n-Undecane	0.5
n-Dodecan-1-ol	n-Dodecane	0.5
n-Tetradecan-1-ol	n-Tetradecane	0.5
3-Phenylpropan-1-ol	n-Propylbenzene	0.7
Secondary		
n-Pentan-2-ol	n-Pentane	0.9
4-Methylpentan-2-ol	2-Methylpentane	0.8
n-Heptan-3-ol	n-Heptane	0.7
2-Methylhexan-3-ol	2-Methylhexane	0.7
4-Methylhexan-3-ol	3-Methylhexane	0.7
5-Methylhexan-3-ol	2-Methylhexane	0.7
2,4-Dimethylpentan-3-ol	2,4-Dimethylpentane	0.7

1	2	3
n-Octan-2-ol	n-Octane	0.6
n-Octan-4-ol	n-Octane	0.6
6-Ethyloctan-3-ol	3-Ethyloctane	0.5
8-Ethyldecan-3-ol	3-Ethyldecane	0.5
Tertiary		
3-Methylheptan-3-ol	3-Methylheptane	0.7
3-Ethylheptan-3-ol	3-Ethylheptane	0.7
Alicyclic alcohols		
Cyclopentanol	Cyclopentane	1.1
Cyclohexanol	Cyclohexane	1.0
3,4-Dimethylcyclohexanol[**]	1,2-Dimethylcyclohexane[***]	0.8
3,5-Dimethylcyclohexanol[**]	1,3-Dimethylcyclohexane[***]	0.8
2-Ethylcyclohexanol[**]	Ethylcyclohexane	0.8
1,3-Dimethylcyclohexanol[**]	1,3-Dimethylcyclohexane[***]	0.9
d,l-i-Borneol	Camphane	0.6
d,l-Menthol	Menthane	0.5
Ketones		
n-Octan-2-one	n-Octane	0.7
Cyclohexanone	Cyclohexane	0.9
Phenyl methyl ketone	Ethylbenzene	0.9

* In all cases the hydrocarbon yield amounted to 93-98%.

** Use was made of mixtures of spatial isomers.

*** The ratio of cis/trans isomers was not determined.

Thus, the catalyst used in our investigation is superior in efficiency to all the known hydrodeoxygenation catalysts. Here we would like to stress upon an important merit of this catalyst: in its presence hydrodeoxygenation takes place at low pressures ($1-2 \cdot 10^5$ Pa).

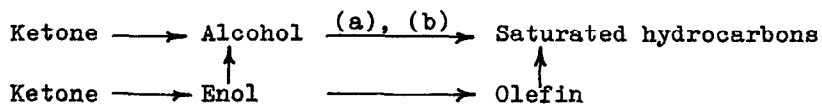At present, the transformation of alcohols into hydrocarbons is considered to proceed in two pathways:

(a) by direct hydrogenation of the C-OH bond;

(b) by dehydration of alcohol into an olefin, followed by hydrogenation to a saturated hydrocarbon.

Lack of necessary experimental data does not permit us to decide between these mechanisms. However, the facts that a fused iron catalyst exhibits low activity during hydrogenation of hexene into hexane[10] and unsaturated hydro-

carbons are not detected among the hydrodeoxygenated products enable us to consider the pathway (a) to be the preferred mechanism.

Hydrodeoxygenation of ketones can proceed as follows:

$$\text{Ketone} \longrightarrow \text{Alcohol} \xrightarrow{\text{(a), (b)}} \text{Saturated hydrocarbons}$$

$$\text{Ketone} \longrightarrow \text{Enol} \longrightarrow \text{Olefin}$$

Our recent observations have revealed that alcohols can be obtained with an almost equal probability both from ketones and their enolic forms.[11] This confirms to some extent the mechanism of deoxygenation of ketones, involving hydrogenation of enols to alcohols.

Details of mechanisms by which alcohols and ketones undergo hydrodeoxygenation in the presence of a fused iron catalyst are now being studied.

The described, highly effective hydrodeoxygenation of alcohols and ketones is of practical interest not only for analytical purposes, but may also be considered as a convenient preparative method of synthesizing different hydrocarbons.

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