Chemistry

1964

SovietRxiv

Abstract

Full Text

Chemistry

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Reduction of High-Molecular-Weight Aliphatic Ketones to Hydrocarbons in the Presence of Aluminosilicate Catalysts

(Presented by Academician B. A. Kazanskii, January 14, 1964)

As is known, the principal pathway for the conversion of ketones over aluminosilicate catalysts in the temperature range 200–250° is the reaction of multistage dehydrating condensation, ultimately leading to the formation of aromatic hydrocarbons.

Alongside this main process, there usually also occur hydration, polymerization, and hydrogen-redistribution reactions, as a result of which acids, unsaturated hydrocarbons, and products of polymerization of the latter are obtained from ketones ([1–7]).

Finally, one could point to another possible pathway for the conversion of ketones, associated with the reaction of direct reduction of the carbonyl group to a methylene group and the formation of the corresponding saturated hydrocarbon with preservation of the carbon skeleton of the initial ketone. However, for such a reaction to proceed, either hydrogen that is active at the moment of liberation is usually required, or else a special hydrogenation catalyst in the case of the action of molecular hydrogen on the ketone.

The reaction of direct reduction of a ketone to the corresponding hydrocarbon in the presence of aluminosilicate catalysts without supplying hydrogen from outside has practically not been investigated. In the literature there is only A. V. Frost' s statement that, when cyclohexanone is boiled with clay at 200–240°, along with other products of ketone decomposition, small amounts of cyclohexane and its isomer methylcyclopentane are formed ([4]).

An important property of aluminosilicates in the reduction of ketones is their ability to stimulate reactions of internal hydrogen redistribution without supplying it from outside. As a result of this reaction, a source of active hydrogen is created, necessary for reduction of the carbonyl group to methylene and conversion of the ketone into the corresponding hydrocarbon.

We have carried out a reaction of this kind using as an example the catalytic conversion of stearone, $C_{17}H_{35}COC_{17}H_{35}$, in the presence of activated clay (gumbrin). Among the other products of catalysis, which represent a mixture of

Fig. 1. IR absorption spectrum of n-pentatriacontane (C35H72)

Figure 1: Fig. 1. IR absorption spectrum of n-pentatriacontane (C35H72)

methane, naphthenic, and aromatic hydrocarbons, a solid paraffin hydrocarbon, *n*-pentatriacontane, $C_{35}H_{72}$, was isolated.

It is quite obvious that it is the product of complete reduction of the initial ketone; however, the mechanism of this process is not yet clear. It is possible that reduction of the ketone proceeds in several stages: first a secondary alcohol is formed, during dehydration of which an unsaturated hydrocarbon is then obtained. Hydrogenation of the latter as a result of the hydrogen-redistribution reaction leads to the formation of paraffin.

The reaction we have investigated—the reduction of high-molecular-weight aliphatic ketones to the corresponding paraffin—also represents considerable ···

considerable geochemical interest. It makes it possible, to a certain extent, to explain the formation of high-molecular solid paraffins in the organic matter of rocks and petroleum from fatty acids that constitute the basis of the original lipid material. In this process, during the ketonic transformation of the acid and the subsequent reduction of the ketone to the corresponding paraffin hydrocarbon, the chain length of the fatty radical of the acid is practically doubled. Also noteworthy is the fact that this reaction is carried out in the presence of clays as potentially possible natural catalysts of the aluminosilicate type.

Experimental Part

The starting stearone was obtained by the method of Esterfield and Taylor [(8)], by heating stearic acid at 320° in the presence of an iron catalyst.

The ketone obtained consisted of white shiny leaflets with a melting point of 89° (literature data: 88.4°).

$C_{35}H_{70}O$. Found, %: C 82.94; H 13.94; O 3.12

Calculated, %: C 83.00; H 13.83; O 3.16

The oxime of stearone melted at 63° (literature data: 62-63°).

Experiments on the catalytic conversion of stearone were carried out at atmospheric pressure, a temperature of 250°, and a heating duration of 6 h. The apparatus and procedure for carrying out the experiment have been described in our preceding studies [(9)].

Fig. 1. IR absorption spectrum of *n*-pentatriacontane ($C_{35}H_{72}$)

In the experiment, 500 g of stearone and 500 g of gumbriin activated with hydrochloric acid were taken.

As a result of catalysis, 431.3 g of oil (86.8% based on the starting ketone) and 21.8 g of high-molecular resins (4.3%) were obtained. The dehydration water amounted to 18.4 g (3.7%).

From the oily part of the catalyzate, a fraction up to 350° was distilled off. The residue above 350°, in an amount of 329.1 g (76.3% based on the catalyzate), was separated by chromatography on silica gel of the ASK grade into a methane-naphthene (82%) and an aromatic (18%) portion.

From the methane-naphthene fraction, which was a solid white mass, by complex formation with urea there was isolated, in an amount of 11%, the solid paraffin—*n*-pentatriacontane. After recrystallization from dearomatized gasoline, the hydrocarbon had the following properties: n_D^{90} 1.4306, d_4^{90} 0.7727; m.p. −75°. According to the literature, the properties of *n*-pentatriacontane are: n_D^{90} 1.4301; d_4^{90} 0.7724; m.p. −74.5°.

$C_{35}H_{72}$. Found, %: C 85.21; H 14.73

Calculated, %: C 85.36; H 14.64

Mol. wt. found 492, calculated 492; MR_D found 163.9, calculated 163.8.

By the formula of Smittenberg [10], the number of carbon atoms in the molecule was calculated and proved to be 35.

For the pentatriacontane obtained, an infrared absorption spectrum was recorded on an IKS-11 spectrophotometer in the region 2-15 μ (5000-670 cm^{-1}).

with an NaCl prism and a layer thickness of 0.05 mm. The spectrum is reported in the literature for the first time.

The spectrum (Fig. 1, Table 1) contains absorption bands of the bending and stretching C—H vibrations of the CH_2 and CH_3 groups, characteristic of methane hydrocarbons of normal structure.

Table 1

Positions of the maxima of the absorption bands of pentatriacontane

λ, μ	ν, cm^{-1}	Intensity	λ, μ	ν, cm^{-1}	Intensity
3.44	2900	s	11.26	890	avg.
3.74	2670	s	13.73	728	s
6.86	1460	s	13.98	715	s
7.24	1380	s			

Splitting of the 720 cm^{-1} band into two is associated with the crystallinity of the hydrocarbon under study.

By the method of Hastings and Andersen (11), a quantitative determination of the CH bonds of the structural groups CH_2 and CH_3 was carried out. The calculations gave the following results: n_{CH2} 34; n_{CH3} 3, with the permissible error of the method being $±$1 group.

The data presented characterize the isolated hydrocarbon as *n*-pentatriacontane.

Thus, as a result of the present investigation, using stearone as an example, the possibility has been shown of reducing ketones to the corresponding hydrocarbons on aluminosilicate catalysts by means of an internal hydrogen-redistribution reaction.

All-Union Petroleum Scientific-Research
Geological-Prospecting Institute

Received
11 I 1964

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Note: Figure translations are in progress. See original paper for figures.