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Abstract

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ON THE COMPOSITION OF ALCOHOLS OBTAINED IN THE LIQUID-PHASE OXIDATION OF *n*-PARAFFIN HYDROCARBONS

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Investigations in the field of liquid-phase oxidation of paraffin hydrocarbons previously led us to develop a directed process for obtaining higher aliphatic alcohols (^{1,2}). The directed character of this process is ensured by the presence of boric acid in the reaction zone and by the choice of reaction conditions.

The study of the chemical composition and structure of the alcohols obtained in this process is of considerable interest for elucidating the mechanism of alcohol formation, as well as for choosing ways of using them rationally. In earlier investigations (^{3}) it was established that, when normal paraffin hydrocarbons are oxidized in the liquid phase by a nitrogen-oxygen mixture containing 3.0-4.5% oxygen, at a temperature of 165-170° in the presence of boric acid, mainly secondary alcohols are formed, possessing the same carbon skeleton and the same number of carbon atoms in the molecule as the starting hydrocarbon. The aim of the present investigation was to clarify the question of the position of the hydroxyl group in the alcohol molecule.

In view of the task posed, our attention was drawn to one of the chemical methods for studying the structure of organic compounds—the method of oxidation of alcohols with potassium dichromate in dilute sulfuric acid medium (^{4}).

When primary alcohols are oxidized by this reagent, carboxylic acids are obtained with the same number of carbon atoms as in the starting alcohol. When secondary alcohols are oxidized, however, rupture of carbon-carbon bonds occurs at the position of the hydroxyl group, as a result of which carboxylic acids with a smaller number of carbon atoms in the molecule are formed. Consequently, from the composition of the acids obtained upon oxidation of alcohols with the indicated reagent, one may judge the position of the hydroxyl group in the alcohols under study. However, there are indications in the literature that this reaction does not proceed entirely smoothly, and that, along with the acids formed as a result of oxidation at the position of the hydroxyl group, acids of another molecular weight are also formed. In addition, when the reaction is carried out in sulfuric acid medium at elevated temperature, certain side reactions occur, leading to resinification. Unfortunately, the question of the quantitative relationship between the main direction of the oxidation reaction and the above-mentioned side reactions has not been sufficiently clarified in the literature.

In order to decide the question of the possibility of applying this method for determining the position of the hydroxyl group in the alcohols under study, we investigated the oxidation reaction of individual aliphatic alcohols with different positions of the hydroxyl group (tetradecanol-4 and hexadecanol-7), followed by identification and determination of the yield of the acids formed. The oxidation of the alcohols was carried out according to the method described—

Kraft for obtaining undecanoic acid from methyl undecyl ketone with minor modifications (^{4}). The weight ratio between the alcohol being investigated and potassium dichromate was 1 : 3. Dilute sulfuric acid (concentration about 50 wt.%) was taken in a tenfold amount relative to the alcohol. In order to avoid deep transformations leading to the formation of side reaction products, the oxidation was first carried out at low temperature (ice cooling), then at room temperature, and finally with heating on a boiling water bath. From the oxidate obtained in the oxidation, the acidic reaction products were isolated through their Na salts. The isolated acids were converted into methyl esters, which were then distilled in a rectification column with a carrier substance (^{5}). A mixture of hydrocarbons purified from olefins and aromatics was used as the carrier. In the fractions obtained, ester numbers were determined, on the basis of which the content of esters in the fractions was calculated. From the boiling ranges of methyl esters of acids of definite composition, it was possible to judge the distribution of the acids formed during the oxidation of the alcohols. The acids were isolated from the methyl esters and then identified by their silver salts.

The data obtained made it possible to establish the presence of definite methyl esters in individual fractions. In addition, on the basis of determining the silver content in the silver salts of the isolated acids, it was also possible to calculate the distribution of the acids. The calculation was made by a formula derived for the case of the possible presence of no more than two acids in a fraction:

$$x = \frac{A(M-1) - 107.9(100-A)}{14A} \cdot 100,$$

where x is the content of acid C_n (mol.%); A is the silver content found in the silver salt (wt.%); M is the molecular weight of acid C_{n+1}.

A study of the oxidation reactions of alcohols with potassium dichromate in dilute sulfuric acid, using as examples several representatives of higher secondary alcohols of the fatty series with different positions of the hydroxyl group, showed that under the conditions adopted by us the yield of reaction products amounts to about 80% of the alcohol taken. The yield of acids is 75% of the isolated reaction products; 25% consists of neutral compounds (mainly ketones).

Investigation of the composition of the acids made it possible to establish that oxidation of the alcohols proceeds mainly (by 90%) at the position of the hydroxyl group. As the hydroxyl group is moved away from the terminal carbon atom, a noticeable deviation from Popov' s rule is observed.

The experimental data obtained give grounds for asserting that the method of oxidizing alcohols with potassium dichromate in sulfuric acid, with subsequent isolation and identification of the acids formed during oxidation, can be used to determine the position of the hydroxyl group in alcohols.

This method was applied by us to determine the position of the hydroxyl group in alcohols obtained by oxidation of *n*-hexadecane. The oxidation conditions and the method of isolating the alcohols were published earlier (^{3}). The main fraction of alcohols, amounting to about 85% of the total amount of isolated monohydric alcohols, was subjected to investigation. This fraction of alcohols was oxidized by the method described above. A certain amount of neutral oxygen-containing compounds (ketones) obtained as a result of the oxidation was oxidized again. The total yield of acids amounted to 96% of the isolated reaction products. Distillation of the methyl esters of these acids made it possible to isolate and identify the following monocarboxylic acids: valeric, caproic, enanthic, caprylic, pelargonic, capric, undecanoic, lau-

valeric, tridecanoic, and myristic acids. It was established that the above acids are present in approximately equal molar ratios (Table 1). Palmitic acid was not detected.

Table 1

Distribution of acids obtained from hexadecanols (oxidation product of *n*-hexadecane)

Acid	By boiling point of the methyl esters, mmol	By boiling point of the methyl esters, %	By silver content in the silver salts, mmol	By silver content in the silver salts, %
Valeric acid ($C_5H_{10}O_2$)	3.52	8.0	3.29	7.5
Caproic acid ($C_6H_{12}O_2$)	3.73	8.5	4.10	9.3
Enanthic acid ($C_7H_{14}O_2$)	5.11	11.5	5.02	11.3
Caprylic acid ($C_8H_{16}O_2$)	4.18	9.5	3.95	9.1

Acid	By boiling point of the methyl esters, mmol	By boiling point of the methyl esters, %	By silver content in the silver salts, mmol	By silver content in the silver salts, %
Pelargonic acid ($C_9H_{18}O_2$)	4.52	10.2	4.52	10.2
Capric acid ($C_{10}H_{20}O_2$)	4.49	10.2	5.42	12.2
Undecylic acid ($C_{11}H_{22}O_2$)	4.52	10.3	4.20	9.5
Lauric acid ($C_{12}H_{24}O_2$)	4.17	9.5	4.50	10.2
Tridecylic acid ($C_{13}H_{26}O_2$)	4.16	9.4	5.20	11.8
Myristic acid ($C_{14}H_{28}O_2$)	4.83	10.9	3.90	8.9
Pentadecylic acid ($C_{15}H_{30}O_2$)	0.87	2.0	–	–

The result obtained makes it possible to conclude that the alcohol fraction studied is a mixture of secondary *n*-hexadecyl alcohols. The possible isomeric alcohols are contained in this fraction in approximately equal molar amounts.

Thus, it has been established that, in the oxidation of *n*-paraffinic hydrocarbons in the liquid phase (in the presence of boric acid), predominantly secondary alcohols are formed, representing a mixture of all possible isomers. No appreciable difference was found in reactivity toward oxygen of the second, third, fourth, etc., secondary carbon atoms of the molecule of higher paraffinic hydrocarbons of normal structure. This gives grounds to believe that, under the oxidation conditions adopted by us, the reactivity toward oxygen of the secondary carbon atoms of the molecule of higher paraffinic hydrocarbons of normal structure is practically the same, which accounts for the formation, in the process of hydrocarbon oxidation, of all possible isomers of secondary alcohols.

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