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Abstract

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ON THE QUESTION OF THE MECHANISM OF ALKYLATION OF PHENOLS BY HIGHER OLEFINS IN THE PRESENCE OF CATION-EXCHANGE RESINS

Cation-exchange resins KU-1, KU-2, SBS, sulfocharcoal, and others, used as catalysts for the reaction of alkylation of phenols by olefins [1–13], are high-polymer sulfonic acids, insoluble but dissociating in the working media with formation of protons [14], and therefore by the nature of their catalytic action they must be identical to sulfuric acid. In alkylation processes in the presence of sulfuric acid, monoalkyl sulfates, which are always present in the reaction mixture because of the readily occurring processes of olefin sulfation, play a definite role in the reaction mechanism. Monosulfates are capable of transesterifying into alkylphenyl ethers, and also of dissociating with formation of carbonium ions prone to substitution of phenol.

Unlike sulfuric acid, cation-exchange resins do not form sulfates with olefins [15], and therefore the formation of carbonium ions from olefins is possible only by addition of a proton, formed in the reaction medium by the cation exchanger, to an unsaturated carbon atom. Thereafter two routes are possible for stabilization of carbonium ions: association with the electron pair of the aromatic nucleus of phenol or with the electron pair of the oxygen atom. In spectral analysis in the infrared region of the products of alkylation of phenol, *o*-, *p*- and *m*-cresols by propylene trimer, bands corresponding to ether bonds are not detected, which indicates the absence of alkylphenyl ethers. This circumstance gives grounds to suppose that in the presence of cation-exchange resins alkylphenols are formed exclusively by substitution in the nucleus. However, according to earlier studies, the processes of obtaining ethers and their rearrangement into alkylphenols under the action of acid catalysts are common to the alkylation reaction of phenols [16–18]. To clarify the applicability of such propositions to the interpretation of the alkylation reaction in the presence of cation-exchange resins, it was expedient to test in this case the possibility of rearrangement of alkylphenyl ethers.

It is known that alkylphenyl ethers with a normal chain and a primary ether-forming carbon atom rearrange with more difficulty than ethers with a branched

Fig. 1. IR spectrum of phenoxyoctane

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Fig. 2. IR spectrum of the third fraction, consisting mainly of *n*-sec.-octylphenol

Figure 2: Fig. 2. IR spectrum of the third fraction, consisting mainly of *n*-sec.-octylphenol

chain and a secondary or tertiary carbon atom [17]. Therefore, for our studies we took phenoxyoctane with a normal aliphatic chain as the most difficult case of rearrangement among high-molecular alkylphenyl ethers.

Phenoxyoctane was obtained by condensation of octyl chloride with sodium phenolate in an alcoholic medium. The constants of phenoxyoctane: boiling point 285–286°, n_D^{20} 1.4895, d_{25}^{25} 0.9081, molecular weight 206—are in good agreement with the literature data [19].

To carry out the rearrangement reaction, phenoxyoctane was passed through a column filled with KU-2 cation exchanger in the H-form at a temperature of 110–115° at a rate of 0.1 g/g of cation exchanger per hour. Similar conditions are used in the alkylation of phenols by higher olefins. In distil-

the reaction products in vacuo on a rectification column with 12 theoretical plates, three fractions were obtained.

First fraction: b.p. 30-45°/20 mm Hg, yield 7.3% of theory, n_D^{20} 1.4090, d_4^{20} 0.7152, mol. wt. 112.3, iodine number 223; it is octene.

Second fraction: b.p. 83-90°/20 mm Hg, yield 8.6%, m.p. 39.4°, mol. wt. 94.6, hydroxyl number 585 mg KOH/g,—mainly phenol.

Third fraction: b.p. 166-174°/20 mm Hg, yield 80.1%, n_D^{20}

Fig. 1. IR spectrum of phenoxyoctane

Fig. 2. IR spectrum of the third fraction, containing mainly *n*-sec.-octylphenol

1.5051, mol. wt. 206, hydroxyl number 272 mg KOH/g; contains mainly *n*-sec.-octylphenol. Similar constants were exhibited by *n*-sec.-octylphenol synthesized by the known method [20] from phenol and normal octyl alcohol in the presence of zinc chloride as catalyst.

Comparison of the absorption spectra in the infrared region of phenoxyoctane and of the third fraction (Figs. 1 and 2) shows that in the former an intense band at 1250 cm^{-1}, corresponding to the ether bond, is clearly observed, whereas in the latter this band has insignificant intensity, indicating the presence of only traces of phenoxyoctane; instead, two bands in the regions 745 and 815 cm^{-1},

characteristic of *n*-sec.-octylphenol [21], are intense, and a band appears in the region 3400 cm^{-1}, corresponding to the presence of an OH group.

Summarizing the experimental results, it may be stated that alkyl phenyl ethers in the presence of cation-exchange resins are rearranged in high yields into alkylphenols, this process being accompanied by decomposition of the ethers into phenol and olefin. The mechanism of these transformations may be represented by two types of reactions: association of a proton with the ether oxygen atom, formation of quinoid structures, and conversion of the latter into alkylphenols

$$\mathrm{PhOR} \xrightarrow{\mathrm{H{-}OSO_2{-}cationite}} \mathrm{PhOR\cdots H} \longrightarrow \text{quinoid intermediate} \longrightarrow \text{alkylphenol}$$

or by dissociation of the alkyl phenyl ether under the action of the cationite into phenol and an unstable primary alkyl cation, which, as a result of bond rearrangement, is converted into an olefin, followed by alkylation of phenol in the ring:

$$\mathrm{C_6H_5O{-}CH_2{-}CH_2{-}R} \xrightarrow{\mathrm{H{-}OSO_2{-}cationite}} \mathrm{C_6H_5OH + R{-}CH_2{-}CH_2^+},$$

$$\mathrm{R{-}CH_2{-}CH_2^+} \xrightarrow{\mathrm{{-}OSO_2{-}cationite}} \mathrm{R{-}CH{=}CH_2},$$

$$\mathrm{R{-}CH{=}CH_2 + C_6H_5OH} \xrightarrow{\mathrm{HOSO_2{-}cationite}} p\text{-}\mathrm{HO{-}C_6H_4{-}CH(CH_3){-}R}.$$

The formation of a secondary alkylphenol from phenoxyoctane is in complete agreement with the second type of reaction, while from the standpoint of an intramolecular rearrangement through quinoid structures it is evidently explained by migration of the benzene ring along the aliphatic side chain.

Alkyl phenyl ethers with a secondary and tertiary carbon atom bound to the phenolic oxygen, whose formation should be expected in the alkylation of phenols with diisobutylene or propylene trimer according to the conditions of electrophilic substitution, dissociate much more readily into phenol and secondary or tertiary cations (more stable than the primary one) and are converted more rapidly into alkylphenols. Therefore, under alkylation conditions, under the action of cation-exchange resins they undergo complete rearrangement into alkylphenols and, as a consequence, are not detected in the reaction products.

On the basis of the foregoing, it should be concluded that in the alkylation of phenols by higher olefins in the presence of cation-exchange resins, as well as other acid catalysts, along with substitution in the ring there occur processes of formation of alkyl phenyl ethers with exhaustive rearrangement into alkylphenols.

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