

## THE APPLICATION OF SULFOCATHIONITE IN ALCYLATION

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*This article is dedicated to the usage of organic ionits as catalysts. According to the modern idea ionits are characterized by insolvent highly moleculated acids and alkalis which are made from monomers by polymerization or polycondensation. The catalytic principle and the mechanism of ionits in the phenol alkylation by olefins are also overviewed here.*

**Introduction.** There is the trend in the catalytic modernization field: liquid catalysts are changed into solids which have advantages in techniques, economy and regeneration.

There are some pivotal benefits of the organic ionits and mineral acids as catalysts:

1. Catalyst can be easily separated from the product by filtration or decantation. It can be used without any regeneration in the process over and over again (for 10 – 15 times). The process based on ionits can be carried out like an uninterrupted circuit.

2. The reaction products are subjected to catalytic both in a porous zone and the solution. Ionits are selective, and that is why adverse reactions are totally expelled. Because of that reason the method mainly matches the production of unstable compounds which are easily biodegradable.

3. Due to the product they are easier to be removed from the reaction zone, there is an opportunity to get a high yield of semi-products in the stepwise reactions. In fact, those semi-products are hardly obtained or none-picked out in a homogeneous catalytic process.

4. In some cases the ion resins application permits to change the way of reaction. Unlike the processes held in dissolved electrolytes (acids, alkyls), as ionits reaction happens with unequal velocity between small and large molecules in accordance to the penetration possibility of reactants throughout ionic porous.

5. Ionits almost do not cause corrosion. [1]

In the 60's a stormy exploration of the phenol alkylation in the presence of sulfocathionits begun. About 60% of alkyl phenol output was obtained by the usage of sulfophenol formaldehyde resins. The same outlet results were achieved with a modern sulfonated copolymer of styrene and divinyl benzene (KU-2) which showed the highest thermal and chemical stability in contrast with sulfonated phenol-formaldehyde resins.

The stationary and elevation bed of catalysts were worked out by Professor V. Izagulianz. The recommended temperatures are 120-130°C. Phenol: olefin ratio is varied from 1:2 to 8:1 mole/mole.

In the late seventies the developments of alkylation on macroporous sulfocathionite appeared. The elevation of the catalytic activity by putting medium or compound modification is widely used.

Organic ionit is employed in different reactions like etherification, acetal synthesis, condensation, alcohols dehydration, esters saponification, alcoholisis and acidosis of eaters.

**Main body.** In this article there is a review of phenol alkylation mechanism on cationits.

Phenol alkylation, as the alkylation of the others aromatics, goes with the removal carbocation substitution to  $sp^2$ -C aromatic ring and carbocomplex formation (fig. 1).

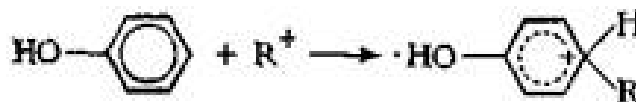


Fig. 1

It is considerable that the alkyl phenol formation has the same further transformation type like the substitution as a result of the proton  $\sigma$ -complex (fig. 2).

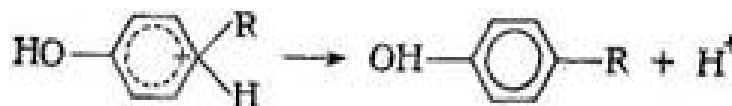


Fig. 2

However, such  $\sigma$ -complex is characterized by a high proton removal activity for hydroxy group. As a result there is a possibility of neutral further readjustment. An essential difference of substitution electrophilic reaction type from others is the transitional alkylcyclohexadiene (fig. 3).

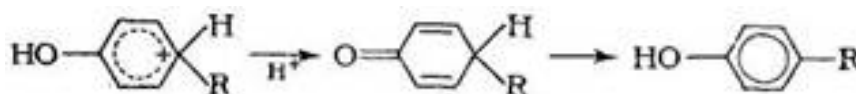


Fig. 3

Generally, phenol alkylation is limited to carbocation derivation. Cyclohexadienon and phenol nucleophile attacks are synchronized. If the synchronization breaks alkyl phenol esters will be derived. Esters are easily isomerized into alkyl phenols by acids.

The neutral pathway mechanism is stable for the account for reaction between olefin and the phenol molecule (fig. 4) [2].

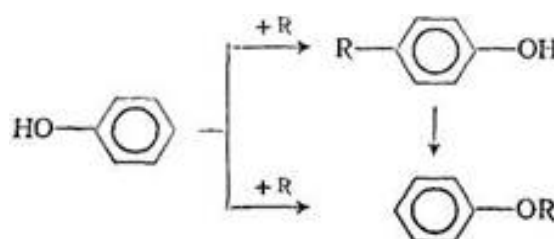


Fig. 4

The reaction pathway leading to direct p-benzenehynon is more energetically favorable than o-benzoquinone. That is the determining factor to faster p-substitution reason.

The major effect in velocity plays the olefin structure. Mono-di- and tri-alkyl phenol forms are coherently alkylations. It's known that hydroxy group interfacing effects cercal density of aromatic and leads to the increase in p-o-positions. Therefore, initial carbonic attack should be directed precisely to these positions. High yields of p-C-alkyl phenol is derived unlike o-C-alkylphenol. With the increase of catalytic activity the temperature and reaction duration of ortho-ratio will be promoted at 60-80% to 95% and more by isomerization.

By the adding of alkyl groups the first reaction step passes faster than the second and that one is faster than the third. Transalkylation has an influence on the composition of compounds. With the increase of catalytic activity the temperature and the reaction duration of the yield of monoalkylphenol increases in the product. For mono-derive one uses equimolar or phenol excess in an initial mixture, for dialkylphenol derive – a mixture with olefin excess.

**Conclusion.** In alkylation there are some unacceptable and unavoidable reactions like:

- Phenol esters derive. In unbeneficial conditions the yield of which rises up to 50% per raw material.
- Olefin polymerization.

As the alkylation has the lowest energy potential (about 21 kJ/mole) the temperature reduction or olefin concentration lessen is prevented from the above reactions.

Thereby the velocity and selectivity of the phenol alkylation depends on the wide range of factors:

- the type and the activity of the catalyst;
- the olefin structure;
- the material ratio;
- the technological factors like the temperature, the duration, the presence of a solvent [3].

As F. Chernishou's experiments showed the phenol alkylation by hexadecane is 1 on Amberlyst - 15 (120°C) 100% alkenes conversion and 97% hexadecylphenol selectivity were reached [4].

Also A. Fakeeu and K. Sadouska in the LLK-Naftan laboratory worked out the other methods of the synthesis with cationic resins, the object was the improvement of the quality and recourse conservation.

Different catalysts were investigated: AMBERLIST 15 DRY RESIN, 35 DRY RESIN, produced by DOW (France); АКБАКОФТ СФЕ 103 DR produced by «Transnov» SIA, Purolite CT 169, Purolite CT175, Puolite CT269 produced by Puolire S.R.L. (Romania), Lewatit K2649 produced by LANXESS (Germany).

According to the investigation made by Lewatit K2649 in alkylation increases the monododecylphenol yield up to 39% and phenol conversion up to 40%. The advantage of Lewatit K2649 is in temperature reduction and conversion increase [5].

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