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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

To the Mechanism of the Isobutane Alkylation with Butenes

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Abstract—-The arguments in favor of a change in the accents at the description of the reaction mechanism of the isobutene alkylation with butylenes in the presence of sulfuric acid are proposed. The reaction of sulfate sulfur reduction that until now considered as the side process is proposed to suggest as just the initiation of chain process which includes generation of *tert*-butyl cations. Such a concept makes it possible to explain a number of characteristic experimental data, in particular failure of attempts of creation of the effective solid catalyst for the alkylation on the basis of the sulfated zirconium oxides.

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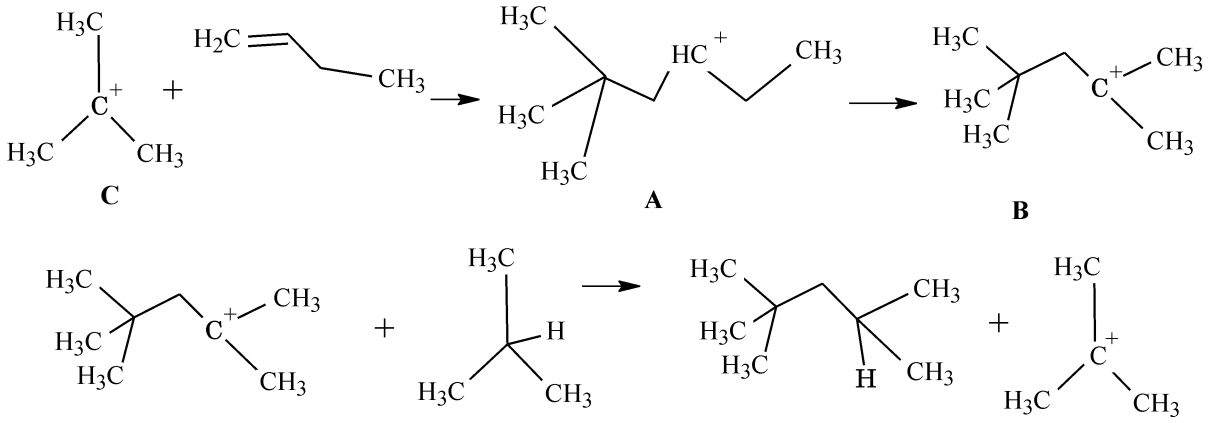
The process of alkylation of isobutane with butenes resulted in formation of alkylate, which is a component of the high-knock rating gasoline, is one of the most important large-capacity petrochemical processes, which acquired recently an even great significance in connection with the introduction of more stringent ecological requirements to the gasoline composition. From the moment of the discovery in the thirties of past century and industrial introduction of this process was attempted creation of a solid catalyst of alkylation instead of concentrated sulfuric acid (98%) and liquid hydrogen fluoride that found industrial application. In the recent decades the reanimation of attempts of obtaining the solid catalyst of the alkylation was connected with the discovery of the high catalytic activity of the systems, obtained, for example, by treatment with sulfuric acid of zirconium oxide, so-called sulfated zirconium [1]. However, in spite of obtaining on the given systems of a catalyzate close in composition to alkylates produced in the industrial installations of alkylation with use of sulfuric acid, all such contact materials are too rapidly deactivating to be considered for industrial application. It should be also accounted for the fact that the problem of their economically reasonable regeneration is not solved. In the described demonstration pilot plants for the alkylation on the solid catalysts, for example, based on BF_3, is organized the continuous additional feeding to the reaction zone of the fresh catalyst.

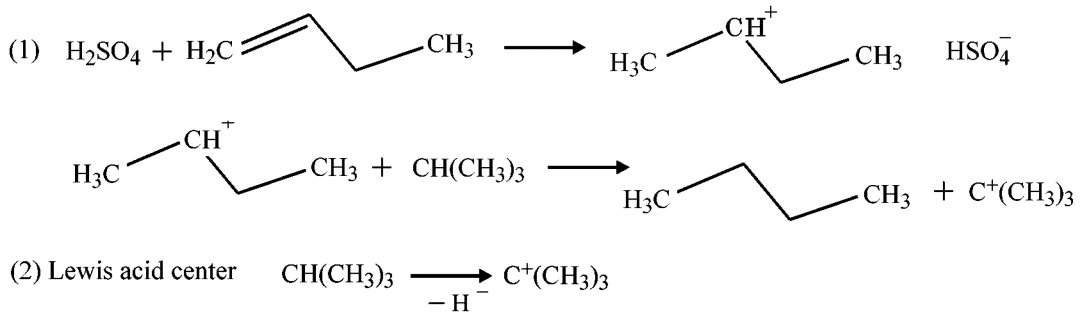
It is suggested that the rapid deactivation of the solid catalysts of alkylation is connected with the blocking of the catalytic centers by the butylenes oligomers formed in the reaction [1]. But even at the liquid-phase sulfuric acid catalyzed alkylation under the industrial conditions it is necessary to feed constantly the reaction mass with fresh sulfuric acid or oleum. In this case at ~ 10°C the mass ratio of organic and acidic phases can be 1:1.5, and isobutane and butylenes ~ 1:7, and the reaction mixture should be effectively stirred. The consumption of sulfuric acid is 5-7 kg per 100 l of alkylate. Such high consumption of catalyst is connected with the side reaction leading to the reduction of sulfates with the elimination of water which dilutes sulfuric acid [2]. The process of alkylation is commonly considered to be the chain ionic process, which is conducted by tert-butyl cations.

Below is given a possible scheme of the reaction of chain propagation, which is accompanied by transfer the hydride ion and methyl anion in the initially formed carbenium ion **A** with interaction of the tert-butyl cation with the butene-1 (Scheme 1). The canceling of this chain, which has small length, taking into account the high comnsumption of catalyst, in essence is connected with

Scheme 1.



Scheme 2.



the transformation of carbocations **A**, **B** and **C** into olefins, the transformation probability grows with decrease in the acidity of acidic phase. This decrease in the acidity occurs during the mentioned reduction of sulfates, which proceeds with the elimination of water.

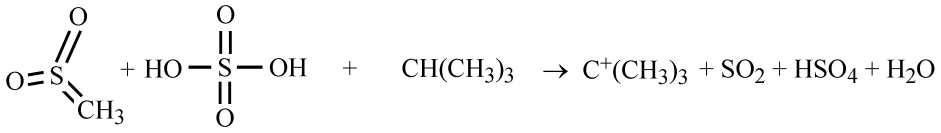
There are two different approaches to the mechanism of the process of tert-butyl cations generation, which is a step of initiation of the considered chain reaction (Scheme 2). The first approach assigns the determining role to the Broensted acidity of active centers, the second to Lewis acidity (Scheme 2).

With such mechanisms of initiation, the reason for small number of cycles at the stage of the reaction chain propagation in the reaction of alkylation catalyzed by sulfuric acid (Scheme 1) is explained by the side reactions, in particular, by mentioned above sulfate the sulfur reductions (Scheme 3). In this case remains the temptation to avoid the side reactions by the creation of the solid catalyst of alkylation. However, the mechanism of alkylation catalyzed with sulfuric acid is not described completely by the schemes like (1) even without taking into account side reactions. For example, for the effective realization of this process is required the formation of so-called red oil, the strongly unsaturated sulfated oligomers, which, as is suggested, are the catalysts of interphase transfer [1].

In our opinion, the explanation of the fundamental problems connected with the high consumption of sulfuric acid at the industrial alkylation and the low resource of the solid catalysts of alkylation on the basis of the sulfated oxides, is absolutely logical when the main reaction, which describes the stage of the chain process initiation, is the given below oxidation-reduction reaction (Scheme 3), which is usually considered as a side-line at the sulfuric acid catalyzed alkylation.

In one of the monographs of Olah, the most widely known authority in the region in question, is contained the statement that the process of the cleavage of a very strong C–H bond with the formation of carbenium ion by thermodynamic reasons is possible only under the condition of the compensating reduction process [3]. One should, however, note that in the same monograph as the stage of initiation of the alkylation of isobutane by butylenes is accepted mechanism 1 (Scheme 2).

Scheme 3.



Since recently the preference is given to the mechanism 2 (Scheme 2). But if we accept the initiation mechanism (Scheme 3) proposed by us, then the deactivation of the catalysts of alkylation on the basis of solid sulfates in question becomes an immanent property, connected with the elimination of water at the stage of initiation. That is, oligomerization of olefins mentioned above is not a cause, but a consequence of catalyst deactivation. Therefore it is not surprising that sulfates at the surface very rapidly lose their activity, and any attempts to noticeably increase the resource of such solid catalysts of alkylation, in principle, are doomed to the failure. On the other hand, it becomes clear why for the effective work of the industrial installations of sulfuric acid catalyzed alkylation is required the stoichiometric amount of acidic phase: in this case the rate of decrease in acidity due to elimination of water diminishes (Scheme 3).

Analogous considerations in the case of alkylation with the use of liquid hydrogen fluoride appear less convincing. Possibly the reaction initiating this process, to which corresponds reaction (Scheme 3), actually is reaction (1).

$$2HF + HC(CH_3)_3 \rightarrow (FHF)^-C^+ + (CH_3)_3 + H_2. \quad (1)$$

This reaction is similar to the proposed by Nenicesku explanation of the catalytic role of aluminum chloride in the analogous reactions [4]:

$$AlCl_3 + HCl + \mathbf{HC}(CH_3)_2 \rightarrow AlCl_4^-C^+(CH_3)_3 + H_2. \quad (2)$$

With this assumed initiation mechanism of the chain process [reactions (1), (2)] it is not understandable in what form the hydrogenation product is accumulated in the reaction mass and how this accumulation specifically contributes to the chain cancellation depicted in the Scheme (1). Substantially, however, that hydrogen fluoride consumption per a unit of the mass of the obtained alkylate is considerably less than consumption of sulfuric acid at the sulfuric acid catalyzed alkylation.

Thus, assuming that in the stage of initiation of chain process at the alkylation proceeds the splitting off the hydride ion from the isobutane molecule, then, without going into details, the basicity of the system as a result of reduction process in this case should grow, which unavoidably should lead to the sufficiently rapid cancel of the chain reaction (1) due to the transformation of carbenium intermediates into appropriate olefins. In this case the regeneration of catalyst via the reoxidation of the restored system in principle is achieved with difficulty, and in practice fresh acids HF, H_2SO_4 adding is required.

Not so long ago has been noted that the resource of the catalyst of alkylation, obtained on the basis of sulfated zirconium, can be increased twice by dosing small quantities of carbon tetrachloride into the zone of the reaction [5]. It is well known that CCl_4 is a very active promotor of the reactions of the reduction of sulfur oxide due to the ease homolysis of C–Cl bond and due to the redox-process leading to formation of phosgene or carbon dioxide [6]. Below is given the modified for the situation a hypothetical reaction of the generation of tert-butyl cations in the presence of carbon tetrachloride, which corresponds to reaction 3 and is analogous to the detaily studied reaction of the carbon tetrachloride–dimethylsulfoxide mixture with reducing agents (very various zerovalent metals) [6].

Hence, during the introduction of carbon tetrachloride a quantity of water eliminated in the step of initiation decreases and, correspondingly, the medium acidity and the activity of the system in the reaction of alkylation fall not so rapidly. If oxidation-reduction reactions 3, 6 are only side processes, then hardly possible to expect a possibility of this reproducible and considerable increase of resource of the solid catalyst of alkylation in the presence of carbon tetrachloride. Thus, if the proposed concept is real, as this is suggested by the author, then, in principle, one should not expect the creation of the effective solid industrial catalyst of the alkylation of isobutane with butylenes from the viewpoint of resource and regenerability.

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