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Mechanism of reaction of *n*-butane with but-2-enes in the presence of LaCaX faujasites

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The reactions of *n*-butane and an *n*-butane (80 mol.%)—isobutane (20 mol.%) mixture with but-2-enes in the presence of polycationic PdLaCaX faujasites were studied. Quantum-chemical calculation of the enthalpies of formation of alkanes C_4—C_8 and their cations showed that the reaction $[Bn^n]^+ \rightleftharpoons [Bu^i]^+$ is of crucial importance for the isomeric composition of the products of alkane alkylation. The general scheme of transformations of the hydrocarbons in the alkylation of *n*- and *iso*-paraffins was proposed based on the experimental data on the distribution of the C_8 isomers in the catalyzate at different temperatures and duration of the reaction.

Key words: *n*-butane, isobutane, but-2-enes, isomerization, trimethylpentanes, dimethylhexanes, X-faujasite, alkylation gasoline, quantum-chemical semiempirical calculations, alkylation.

The growth of the world automobile fleet and related ecological problems require the exclusion of toxic lead-based antiknock additives from gasoline and lowering the content of aromatic hydrocarbons. Therefore, an increase in the production of alkylation gasoline, which presently takes approximately one seventh of the total gasoline produced in the world, is urgent. The most part of alkylation gasoline is manufactured[1—5] by the reaction of isobutane with olefins C_2—C_5 in the presence of H_2SO_4 or HF. These methods have a serious disadvantage: formation of poorly utilizable acidic tars and the use of only *iso*-paraffins as raw materials. In this connection, the development of new processes using heterogeneous catalysts becomes more important. Such processes are more environmentally safe, and they can involve unbranched paraffins, in particular, *n*-butane, in alkylation reactions especially because the supply of the latter substantially exceed resources of deficient isobutane.[6] A study of the mechanism of transformations of *n*-paraffins in the presence of olefins is of special interest. A comparative analysis of the behavior of *n*- and *iso*-paraffins in alkylation makes it possible to evaluate the present concepts on the specific features of particular stages in traditional mechanisms of these reactions and check the adequacy of the description of the real routes of *n*-alkane transformations by these concepts.

Experimental

The catalysts were based on zeolites X (faujasites), which are well known in petrochemistry, much more sensitive to elevated temperatures than high-silica Y-faujasites,[7] and characterized by the maximum activity in alkylation. The $La_{0.18-0.22}Ca_{0.21-0.15}Na_{0.04}[(Al_1Si_{1.40})O_{4.80}]\cdot nH_2O$ catalysts were prepared by ion exchange of the starting NaX form with solutions of calcium and lanthanum nitrates.

Palladium (0.3—0.5 wt.%) was introduced into these samples by ion exchange. A mixture of 70 wt.% zeolite and 30 wt.% pseudoboehmite was extruded and thermally treated at 450 °C. The resulting catalyst was tested in a riser reactor with the ascendant stock flow.

The following starting products were used: (1) a mixture of *n*-butane and isobutane obtained by *n*-butane isomerization on zeolites with similar composition at 300 °C (content of isobutane was 20—25 mol.%)[8] with an additive of but-2-enes (2 wt.%) with respect to the total weight of hydrocarbons and (2) a mixture of *n*-butane and but-2-enes with the 50 : 1 weight ratio.

Experiments were carried out in the 50—150 °C temperature range. The pressure (*P*) was maintained at a level of 4.0—5.0 MPa to keep the raw materials in the liquid-phase state in the reaction zone. The space feed rate for the alkylation of a mixture of isobutane and *n*-butane (hereinafter named the isomerizate) was 4 h^{-1}, and that for *n*-butane alkylation was 2 h^{-1}.

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Reaction products were analyzed by GLC using an Ekokhrom-93 program-apparatus complex consisting of a Hewlett Packard 5709 chromatograph with a flame-ionization detector and an analog-to-digital converter. The CHROM 1.0 for Windows program was applied in calculations.

The enthalpies of formation (ΔH_f) for isomeric paraffins C_4 and C_8 and their cations were calculated by the quantum-chemical PM3 method using the HyperChem PC program.

Results and Discussion

The temperature plots of the conversion, the relative yield of the liquid product, and the content of hydrocarbons C_8 in the reaction products are extremal, and the position of the extreme in the temperature scale are approximately the same in all cases (Fig. 1). A substantial difference in the reaction temperatures at which the maximum catalyst activity is achieved (125 °C for *n*-butane and 75 °C for the isomerizate) indicates that *n*-butane is much less reactive than its mixture with isobutane. These data allow one to compare the ease of hydride ion elimination from the tertiary and secondary C atoms of the *n*-butane molecule.

The features of particular stages of paraffin alkylation by olefins have been studied in detail in recent decades.[1—5,8—17] Many researchers agree that the mechanism proposed by Schmerling[9—11] correctly reflects, as a whole, the essence of processes during paraffin alkylation by olefins despite some incompleteness and inaccuracy. According to this mechanism, the alkylation of isobutane with *n*-butenes affords a mixture of different trimethylpentanes (TMP) (mainly 2,2,4-TMP, 2,2,3-TMP, 2,3,4-TMP, and 2,3,3-TMP). This conclusion was confirmed in many works on isobutane alkylation with

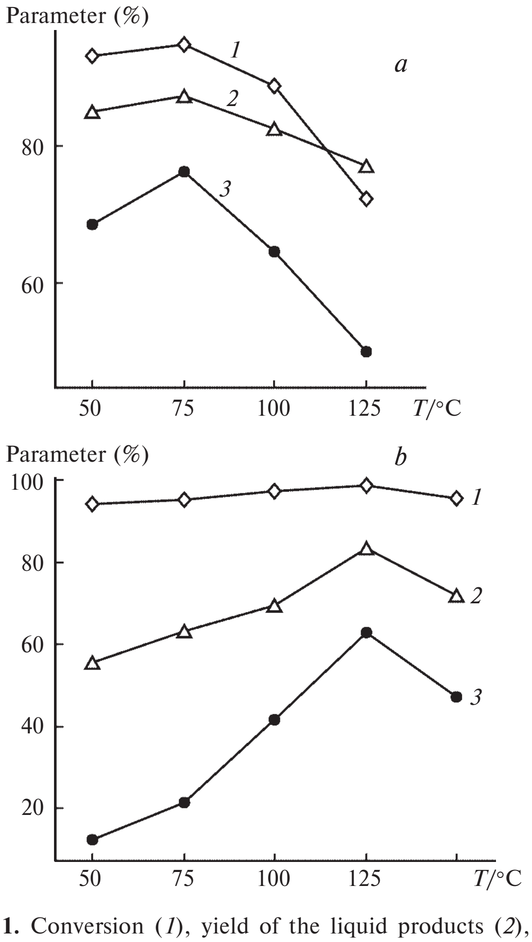


Fig. 1. Conversion (*1*), yield of the liquid products (*2*), and content of hydrocarbons C_8 in the reaction products (*3*) as a function of the temperature of alkylation of the isomerizate (*a*) and *n*-butane (*b*) with but-2-enes on PdLaCaX-faujasites (P = 4.0 MPa, the first h of the catalysts working).

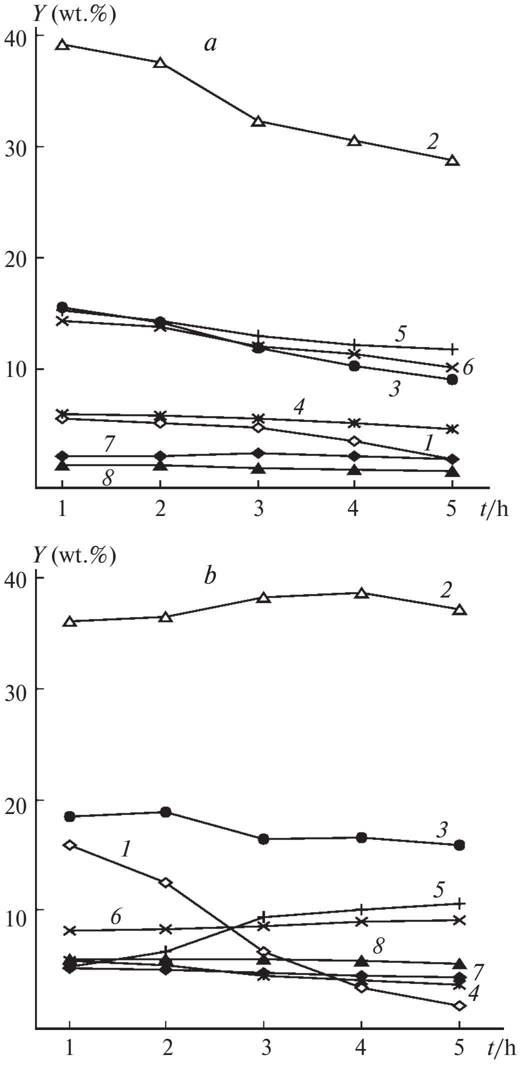


Fig. 2. Content (*Y*) of 2,2,4- (*1*), 2,3,3- (*2*), 2,3,4- (*3*), 2,2,3-TMP (*4*), 3,4- (*5*), 2,4- (*6*), 2,5- (*7*), and 2,3-DMH (*8*) in the fraction C_8 as a function of time of the catalyst working (*t*) for the alkylation of *n*-butane (*a*) and isomerizate (*b*) with but-2-enes on PdLaCaX-faujasites at 125 (*a*) and 75 °C (*b*) (P = 4.0 MPa).

Table 1. Content of trimethylpentanes (TMP) and dimethylhexanes (DMH) in products C_8 formed by the alkylation of *n*-butane and isomerization (figures in parentheses) with but-2-enes on PdLaCaX faujasites

T/°C	Content of isomer (wt.%)							
	2,2,4-TMP	2,3,3-TMP	2,3,4-TMP	2,2,3-TMP	3,4-DMH	2,4-DMH	2,5-DMH	2,3-DMH
50	3.2 (11.4)	38.0 (42.4)	12.7 (23.6)	3.3 (4.7)	14.4 (4.3)	11.9 (4.3)	6.6 (2.2)	3.9 (6.1)
75	3.3 (15.8)	37.9 (36.1)	12.4 (18.5)	3.8 (5.4)	14.8 (4.9)	12.2 (8.1)	6.2 (4.8)	3.5 (5.5)
100	3.6 (16.3)	39.1 (34.7)	15.5 (18.1)	5.5 (5.0)	14.9 (5.3)	13.8 (10.0)	5.5 (5.1)	2.1 (5.3)
125	5.5 (17.5)	39.2 (32.1)	15.5 (17.1)	5.9 (4.1)	15.3 (6.0)	14.3 (11.9)	2.1 (5.7)	1.4 (5.0)
150	6.2	38.3	15.1	6.3	16.2	15.2	1.9	0.6

n-butenes in the presence of liquid and heterogeneous catalysts.[1—5,8—17]

Accepting such a scheme for *n*-butane, we see that the main reaction products should be dimethylhexane (DMH) isomers (mainly 3,4-, 2,4-, 2,2-, and 2,5-DMH). However, according to the data in Table 1 and Fig. 2, *a*, the total amount of TMP in *n*-butane alkylation with but-2-enes on PdLaCaX-faujasites is 1.2—2.0 times greater than the amount of DMH isomers. Thus, *n*-butane alkylation affords the products, whose isomeric composition does not correspond to the Schmerling mechanism.

It can be assumed that *n*-butane is partially isomerized to isobutane, which is much more reactive than *n*-butane, and this is precisely isobutane which really reacts. However, this assertion meets the objection that the TMP/DMH ratio increases with the temperature increase to ~125 °C (Fig. 3, curve *1*) (along with this, the yield of the liquid products also considerably increases, see Fig. 1, *b*), although the temperature increase should be accompanied by the enhancement of TMP isomerization to more thermodynamically stable DMH. Therefore, the TMP/DMH ratio should more likely decrease with temperature, as it takes place in the alkylation of the isomerizate (see Fig. 3, curve *2*).

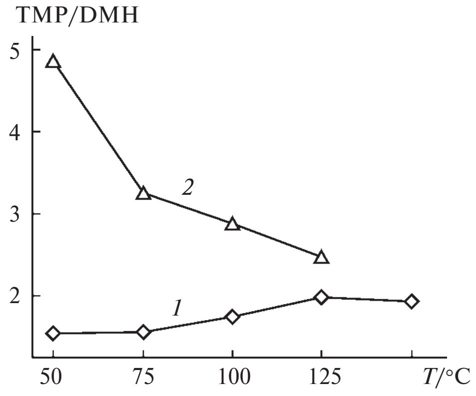


Fig. 3. TMP/DMH ratio as a function of the temperature of alkylation of *n*-butane (*1*) and isomerizate (*2*) with but-2-enes on PdLaCaX faujasites (*P* = 4.0 MPa).

In order to explain this unusual, at first glance, result, we advanced several assumptions concerning particular pathways of *n*-butane transformations, which could give the experimentally observed isomeric composition of the reaction products.

1. *n*-Butane is isomerized to isobutane before its transformation into the *n*-butyl cation. Thus, the isobutyl cation formed from isobutane reacts instead of the *n*-butyl cation (*e.g.*, according to the Schmerling mechanism). The DMH isomers can form by both the direct alkylation of *n*-butane with but-2-enes and isomerization of all possible TMP and TMP^+ (TMP^+ are isomerized to DMH^+, and the latter are transformed into DMH), as well as by the alkylation of isobutane with *n*-but-1-ene formed from but-2-enes.

2. The TMP isomers are formed due to the isomerization of all possible DMH^+ (DMH^+ are isomerized to TMP^+, and those are transformed into TMP), which, in turn, are the products of addition of the *n*-butyl cation to the but-2-ene molecules. The formation of TMP from DMH is improbable because the most of DMH isomers are thermodynamically more stable than TMP under the experimental conditions.

3. The *n*-butyl cation is isomerized at the moment of formation (when a hydride ion is eliminated from the *n*-butane molecule) to the isobutyl cation. The further transformations of the isobutyl cations occur in approximately the same manner as it is described in point 1 (like the formation of the DMH isomers).

The first assumption is rejected by the results of studying[8] *n*-butane isomerization, according to which it does not virtually occur on the catalysts at temperatures <200 °C.

In order to verify two other assumptions, we compared the experimental data (see Figs. 1—3, Table 1) with the results of quantum-chemical calculation of the enthalpy of formation of the isomeric paraffins C_4, DMH, TMP, and their cations (Table 2).

As known, the rearrangements of the carbocations under discussion are characterized by rather low activation energies (~10 kcal mol^{-1}). Therefore, based on the enthalpy of rearrangements of different carbocations, one can predict (with an accuracy sufficient for qualitative

Table 2. Enthalpies of formation (ΔH_f) of isomeric paraffins C_4, DMH, TMP, and their cations calculated by the PM3 method

Paraffin	ΔH_f/kcal mol^{-1}	
	Molecule	Cation*
n-Butane	−29.76	178.59 (2)
Isobutane	−31.41	190.61 (2)
2,3-DMH	−51.65	155.59 (2), 155.88 (3), 169.43 (4), 165.98 (5)
2,4-DMH	−52.40	154.19 (2), 169.58 (3), 155.17 (4), 166.22 (5)
2,5-DMH	−53.02	153.05 (2), 167.11 (3)
3,4-DMH	−51.07	168.14 (2), 157.50 (3)
2,2,3-TMP	−52.41	156.44 (3), 169.47 (4)
2,2,4-TMP	−53.62	171.63 (3), 153.70 (4)
2,3,4-TMP	−51.92	156.54 (2), 158.03 (3)
2,3,3-TMP	−51.68	157.64 (2), 171.26 (4)

* The position of the C atom on which the charge is localized in indicated in parentheses.

evaluation) the main reaction routes and prevailing isomers in the reaction products.

Several important conclusions can be drawn from the data presented in Table 2.

First, carbocations, whose charge is localized on the tertiary C atom, are, as a rule, more stable than the corresponding cations with the charge on the secondary C atoms (by at least 10 kcal mol^{-1}). Therefore, these cations should isomerize, immediately on their formation, to cations with the charged tertiary C atoms. Remind that according to the Schmerling mechanism,[9—11] the 2,2,3-TMP$^+$ cation with the charge on the C(4) rapidly isomerizes at the moment of formation to the more stable tertiary TMP cations.

Second, our results reject the assumption that the TMP isomers are formed from the cationic DMH. Almost all DMH$^+$ ions with the charged tertiary C atom are more stable than similar TMP$^+$ ions (except for the structures in which the methyl groups in DMH$^+$ are next to each other), although the difference is usually only 1—2 kcal mol^{-1}. Therefore, it is assumed that the TMP$^+$ to DMH$^+$ rearrangements do not either predominate.

The third and most important conclusion the completely confirms our third assumption. The absolute value of the enthalpy change ($|\Delta H|$) in the $[Bu^n]^+/[Bu^i]^+$ cation rearrangement (with the charge on the C(2) atom) is the highest among the corresponding values for all the most possible rearrangements and equals 12.02 kcal mol^{-1}.

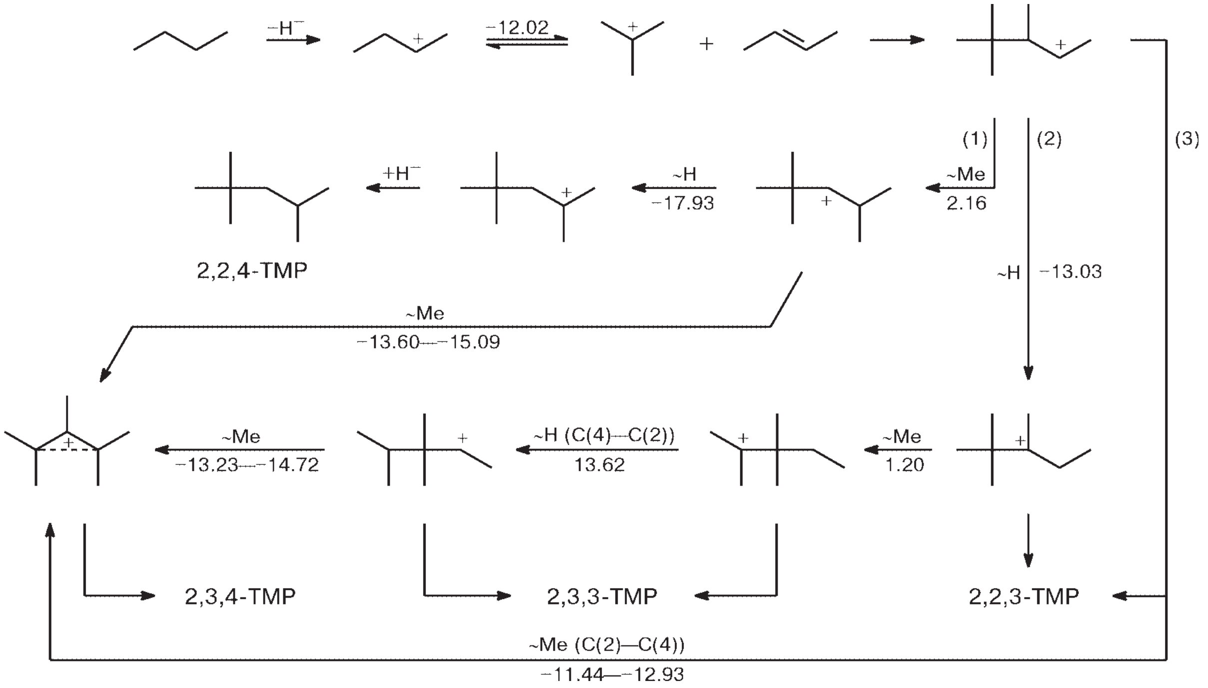
Thus, the butyl cations formed by hydride ion elimination from the *n*-butane molecule can isomerize to isobutyl cations yet before addition to the but-2-ene molecules. The rate of approaching the reversible reaction $[Bu^n]^+ \rightleftharpoons [Bu^i]^+$ (with the charge on the C(2) atom) to the thermodynamic equilibrium increases with temperature. This results in an increase in the conversion of the butyl cation to the thermodynamically more stable isobutyl cation. However, since the addition of the isobutyl cation to but-2-enes and subsequent transformations afford trimethylpentanes (unlike these, *n*-butyl affords dimethylhexanes), their content in the alkylate increases with temperature. The TMP/DMH ratio also increases (see Fig. 3).

The further temperature increase is accompanied by the maximum approach of the $[Bu^n]^+ \rightleftharpoons [Bu^i]^+$ transformation to the thermodynamic equilibrium, due to which the $[Bu^i]^+/[Bu^n]^+$ ratio stops increasing. However, the degree of isomerization of all possible TMP$^+$ and TMP isomers to thermodynamically more stable DMH$^+$ and DMH increases. This results in a decrease the TMP/DMH ratio and the appearance of an insignificant maximum in the plot of this quantity *vs.* temperature of *n*-butane alkylation by but-2-enes (see Fig. 3).

However, numerous studies did not reveal the specific routes of the mutual transformations of the cationic TMP$^+$ and DMH$^+$ intermediates, which finally defines the isomeric composition of the reaction products. According to the data in Table 3, the enthalpies of formation of all the most stable TMP$^+$ and DMH$^+$ cations are very close, which does not allow a certain conclusion about the predomination of particular reaction pathways. At the same time, it is seen in Table 1 and Fig. 2 that when either *n*-butane or the isomerizate are used as the raw materials, a correlation between the concentrations of 2,3,3-TMP and 2,3,4-TMP in the reaction products is observed. Meanwhile, no similar correlation between the contents of these isomers and 2,2,4-TMP exists. This fact allows us to conclude that these hydrocarbons are formed *via* different reaction routes (Schemes 1 and 2, ΔH/kcal mol^{-1} for cation rearrangements are indicated by figures in Scheme 1).

The addition of the isobutyl cation with the charge on the C(2) atom to the but-2-ene molecule affords the 2,2,3-TMP cation with the charge on the C(4) atom, which can further transform *via* three main routes (see Scheme 1). The most probable are pathways (2) and (3), which provide the maximum energy gain at the very first stages (ΔH for them are −13.03 and −11.44 to −12.93 kcal mol^{-1}, respectively). This conclusion is confirmed by our experimental data, according to which the

Scheme 1

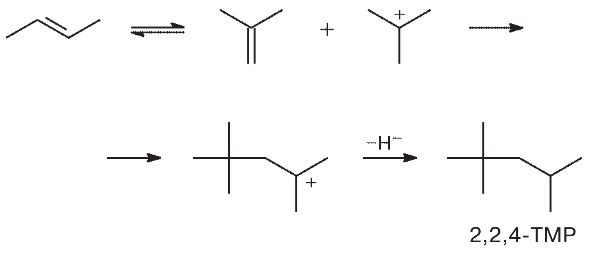


alkylation of *n*-butane and the isomerizate with but-2-enes affords most 2,3,3-TMP of the TMP isomers (route (2)) and somewhat less (by 1.5—3.0 times) 2,3,4-TMP (route (3)). The latter can be explained by the fact that for similar rearrangements the rate of hydride transfer is much higher than that of methyl transfer (this is precisely the difference between routes (2) and (3)).

The existence of a single intermediate through which 2,3,3- and 2,3,4-TMP are formed gives an insight into the same ratio between these isomers during the whole testing period of catalysts (see Fig. 2).

Unlike 2,3,3- and 2,3,4-TMP, the most amount of 2,2,4-TMP is formed, most likely, according to Scheme 2 involving isobutylene as an olefin. This is indicated by the absence of a correlation between the amounts of 2,3,3- and 2,3,4-TMP that formed, on the one hand, and 2,2,4-TMP, on the other hand, and also by the parallel change in the content of isobutylene (as well as isobutane) and 2,2,4-TMP in the reaction products. However, a certain contribution of reaction pathway (1) in Scheme 1 cannot either be excluded.

Scheme 2



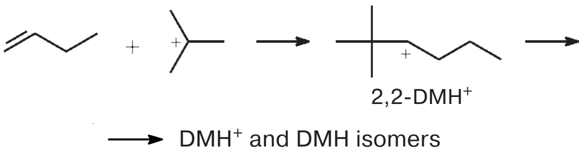
The DMH isomers are also formed *via* different routes, depending on a paraffin reacting with olefins at the first stage of the reaction. Scheme 3 mainly corresponds to the formation of the DMH isomers when *n*-butane is used as a paraffin. This is indicated by the high content of 3,4-DMH in the reaction products (see Table 1, Fig. 2, *a*), which increases with temperature due to the intensification of alkylation (see Table 1).

Scheme 3

When the isomerizate containing a sufficient amount of isobutane is alkylated, the DMH isomers are likely formed predominantly according to Scheme 4. This is indicated by the high content of 2,3-DMH in the alkylation products (see Table 1, Fig. 2, *b*) because 2,3-DMH is formed immediately from 2,2-DMH with the charge on the C(3) atom.

Thus, the study of the alkylation of *n*-butane and *n*-butane—isobutane mixture obtained by *n*-butane

Scheme 4



isomerization (isomerizate) in the presence of the LaCaX faujasite catalyst suggests that the traditional models of alkylation mechanisms cannot adequately describe the transformation of unbranched paraffins. The enthalpies of formation (ΔH_f) of several isooctanes and their cations, which play an important role in the stages of transformation of the starting to final products, were calculated by the quantum-chemical semiempirical PM3 method and showed a satisfactory correlation between ΔH in the stages of carbocationic rearrangements and their relative contributions to the overall transformation of the starting hydrocarbons. Several principal schemes were proposed for the mechanisms of the reactions. As a whole, they describe satisfactorily the isomeric composition of the products.

An important role of the mutual transformation

was concluded. This transformation affects both the isomeric composition of the reaction products and the qualitative parameters of the process (conversion of olefins, the yield of the liquid product, TMP/DMH ratio, and, as a consequence, the octane number of the alkylate obtained). The increase in the TMP/DMH ratio with temperature of the reaction on PdLaCaX-faujasites is caused by the shift of the indicated equilibrium toward the thermodynamically more stable isobutyl cation. The 2,3,3- and 2,3,4-TMP isomers, on the one hand, and 2,2,4-TMP, on the other hand, are formed *via* different reaction routes but, in all cases, the single initial intermediate exists, *viz*., 2,2,3-TMP cation with the charge on the C(4) atom, which is the product of the direct addition of the isobutyl cation to the but-2-ene molecule. The DMH isomers are also formed through different reaction pathways. When *n*-butane is the starting material, the reaction involves 3,4-DMH and its cations. When isobutane in the composition of the isomerizate is used, the products are formed *via* 2,2-DMH formation (main intermediate is the 2,2-DMH cation with the charge on the C(3) atom).

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References

1. L. Schmerling, in *Khimiya uglevodorodov nefti* [*Chemistry of Petroleum Hydrocarbons*], Gostoptekhizdat, Moscow, 1959, **3**, 305 (Russ. Transl.).
2. US Pat. 2888500; *Chem. Abstrs.*, 1959, **53**, 16524a.
3. A. Z. Dorogochinskii, A. V. Lyuter, and E. G. Vol´pova, *Sernokislotnoe alkilirovanie izoparafinov olefinami* [*Sulfuric Alkylation of Isoparaffins with Olefins*], Khimiya, Moscow, 1970, 216 pp. (in Russian).
4. T. Hatson and D. E. Heis, in *Alkilirovanie. Issledovanie i promyshlennoe oformlenie protsessa* [*Alkylation. Study and Industrial Design of the Process*], Khimiya, Moscow, 1982, 33 (Russ. Transl.).
5. V. G. Telegin, V. A. Kobelev, and D. V. Mushenko, *Tr. Vsesoyuzn. NII neftekhim. protsessov* [*Proceedings of the All-Union Research Institutes of Petrochemical Processes*], 1960, issue 3, 193 (in Russian).
6. A. I. Bogomolov, A. A. Gaile, and V. V. Gromova, in *Khimiya nefti i gaza* [*Oil and Gas Chemistry*], Khimiya, Moscow, 1995, 145 (in Russian).
7. W. E. Garwood and P. B. Venuto, *J. Catal.*, 1968, **11**, 175.
8. A. L. Bachurikhin, V. A. Plakhotnik, and E. S. Mortikov, *Neftekhimiya*, 1999, **39**, 113 [*Petrochemistry*, 1999, **39** (Engl. Transl.)].
9. L. Schmerling, *J. Am. Chem. Soc.*, 1945, **61**, 1152.
10. L. Schmerling, *Ind. Eng. Chem.*, 1948, **40**, 2072.
11. K. I. Patrilyak, Yu. N. Sidorenko, and V. A. Bortyshevskii, *Alkilirovanie na tseolitakh* [*Alkylation on Zeolites*], Naukova Dumka, Kiev, 1991, 176 pp. (in Russian).
12. J. E. Hofmann and A. Schriesheim, *J. Am. Chem. Soc.*, 1962, **84**, 953.
13. J. E. Hofmann, *J. Org. Chim.*, 1964, **29**, 1497.
14. L. F. Olbrait, B. M. Dosin, and M. A. Ferman, in *Alkilirovanie. Issledovanie i promyshlennoe oformlenie protsessa* [*Alkylation. Study and Industrial Design of the Process*], Khimiya, Moscow, 1982, 87 (in Russian).
15. A. Martines, A. Martines, and C. Martines, *Catal. Rev., Sci. Eng.*, 1993, **35**, 483.
16. J. Weitkamp and S. Maixner, *Chemie*, 1983, **36**, 11.
17. J. Weitkamp, *Proc. Intern. Symp. on Zeolite Catalysis, Zeocat´85*, Siofok (Hungary), 1985, 690.

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