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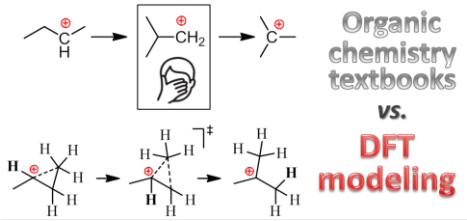
Rearrangements of carbocations during isomerization and oligomerization of hydrocarbons: is it time to dot the 'i'?

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The mechanisms of the rearrangements of carbocations, usually discussed within college courses in organic chemistry, are often superficial and incomplete. In this feature article, we discuss development of ideas about the reaction mechanisms and up-to-date understanding of the pathways of similar processes using high-level DFT modeling. Additionally, we present how fast DFT simulations (PRIRODA software) foster visualization and understanding of carbocation transformations.



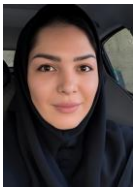
Keywords: carbenium ions, carbocations, DFT, isomerization, olefins, oligomerization.



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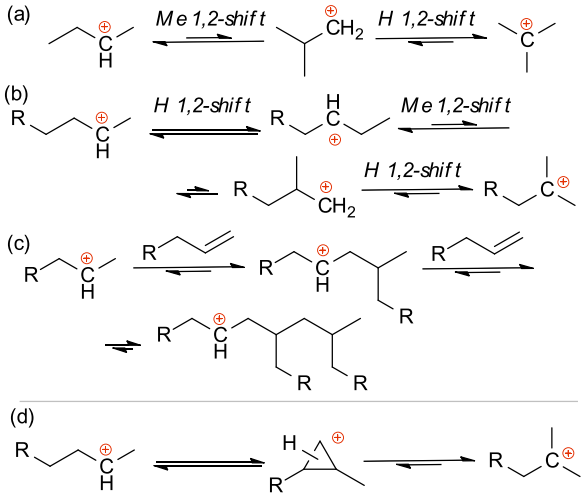
Ilya E. Nifant'ev received his Ph.D. degree (1988) and DSc. degree (1992) at the Department of Chemistry, M.V. Lomonosov Moscow State University. His current status is Professor of Organic Chemistry at Moscow University, and Head of the Laboratory for Organometallic Catalysis at the A. V. Topchiev Institute of Petrochemical Synthesis RAS. His main research interests are catalytic transformations of α-olefins, dienes, cyclic esters and renewable raw materials, synthesis of fine chemicals, and development of actual materials for biomedical applications. Prof. Nifant'ev is a member of the Editorial Board of Petroleum Chemistry journal.

Isomerization of carbocations: practical, theoretical and methodological aspects

Isomerization of hydrocarbon chain accompanies numerous processes of modern oil refining and petroleum chemistry, e.g. catalytic isomerization and cracking of paraffins,[1,2] butenes → isobutylene (IB) isomerization,[3] acid-catalyzed oligomerization of IB[4] and α-olefins.[5] In many cases, carbocations are reactive intermediates of similar processes. Therefore, it is quite obvious that understanding of the mechanisms of rearrangements of carbocations is of great theoretical and practical interest.

If we turn to basic college (and even university) organic chemistry courses, we often observe reaction schemes designed to simplify understanding of the reaction mechanisms (Scheme 1a–c; see also Figure S1 in the Online Supplementary Materials). In advanced courses in organic chemistry, protonated cyclopropane intermediates are examined and discussed after all, at least for secondary carbenium ions (Scheme 1d), but IB formation, IB oligomerization, and α-olefin oligomerization remain beyond discussions.

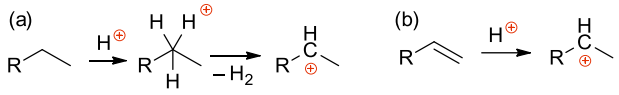
The tremendous importance of cationic rearrangements in oil processing, petroleum chemistry and fine chemistry require a thorough understanding of the mechanisms of similar reactions. Development of new catalysts and products, optimization of existing technologies and creation of new industries impose new requirements to chemical education. This mini-review combines discussion of core and relevant conceptions of the reaction mechanisms, catalytic solutions and product ranges. In addition, the present work contains elements of research: to clarify controversial mechanistic statements and hypotheses, we added a number of vivid examples from our research practice, including the results of DFT modeling. The final sections strengthens a tutorial facet of this work and outlines the objectives of the future investigations.



Scheme 1 Simplified mechanisms of the key stage of but-1-ene → isobutylene isomerization (a), cationic rearrangements during catalytic isomerization of linear alkanes (b), and cationic oligomerization of α-olefins (c). Mechanism of rearrangement of secondary alkyl cations *via* protonated cyclopropane (d).

Theoretical concepts of the formation and rearrangements of carbocations: past and present

First, let us define the main possible ways of the formation of carbenium ions from hydrocarbons, namely protonation/dehydrogenation of alkanes and protonation of the olefins (Scheme 2).



Scheme 2 Two main ways of the formation of carbenium ions from hydrocarbons: protonation/dehydrogenation of alkanes and protonation of olefins.

Protonation of alkanes with a formation of carbonium ions† is an inevitable stage of acid-catalyzed isomerization of paraffins,[6] but this important reaction is often only mentioned in the academic literature. The simplest example of protonation of alkane molecule is a formation of CH_5^+ ion. Since the discovery of CH_5^+ in 1952 by Tal'roze and Lyubimova,[7] the structure of CH_5^+ has been a subject of numerous discussions and speculations.[8] In simple words, the crux of the problem is the tension between the

† Note that in early publications the term "carbonium ion" was applied to all carbocations. In the current IUPAC nomenclature carbonium ion is a cation that has a pentacoordinated carbon atom.

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conventional notions that describes CH_5^+ as an adduct of CH_3^+ and H_2 (Figure 1a) and experimental studies that revealed dynamic behavior of this molecule, which leads to equivalence of the C–H bonds.[9] The CH_5^+ molecule has been considered as a chemistry's "Cheshire Cat".[10] Experimental and theoretical studies of this mysterious molecule continue today.[11]

To illustrate quantum-chemical approach to addressing molecular structure of CH_5^+, we performed 20-second DFT modeling using PRIRODA program [12] (T = 298.15 K, gas phase, PBE functional, 3ζ basis set, Intel Core i7-6700HQ, 8 Gb RAM; calculated energies and optimized geometry are presented in Online Supplementary Materials). The results of this fast DFT visualization correlate with the structures presented in Figure 1a. Also note that these results are not contrary to those generated using more advanced and resource-intensive methods. [8,10,11,13]

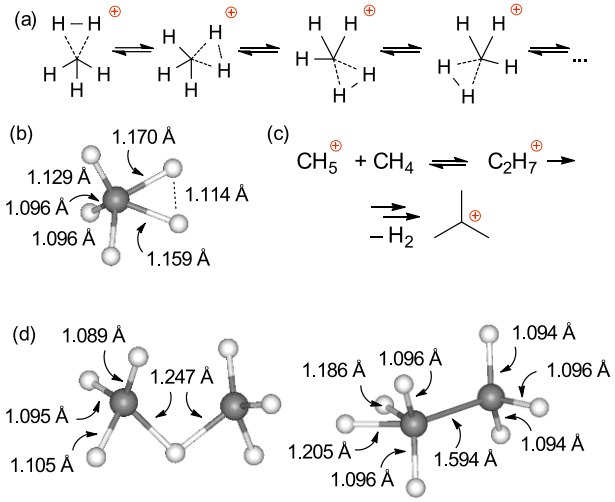


Figure 1 The common view of the CH_5^+ as a dynamic CH_3^+–H_2 adduct (a); optimized geometry of CH_5^+ (b, this work); chemical behavior of CH_5^+ in CH_4 medium (c); optimized geometries of $C_2H_7^+$ species (d, this work).

CH_5^+ is a highly reactive molecule. Back in 1969,[14] Olah and coll. showed that CH_5^+ react with CH_4 with a formation of protonated ethane as an intermediate, the reaction continues until formation of ^{t}Bu$^+$ (Figure 1c). This extremely promising reaction, however, has not yet found practical implementation. Our DFT optimization revealed two stationary points for $C_2H_7^+$ (Figure 1d), protonated ethane turned out to be less stable than μ-H-bridged structure (ΔG = 4.3 kcal·mol^{-1}, see SM) – maybe, that is the point. The results of this fast modeling correlate with the data reported previously by Collins and O'Malley.[15]

It is worthwhile mentioning that intermediate formation of carbonium ions is not necessarily the indispensable stage of alkane activation: in 2012, calculations of Dinér revealed a transition states without local minima in reaction between $HSbF_6$ and alkanes (see example in Figure 2).[16] However, recent mechanistic studies of alkane activation in zeolites showed that carbonium ions are still formed under similar industrially relevant conditions.[17,18]

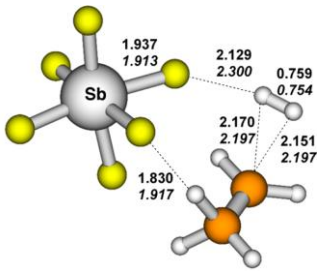


Figure 2 Optimized structure and the most important geometric parameters of the transition state for protolytic C−H bond cleavage at the B3LYP/6-311+G(d,p) (normal) and M062X/6-311+G(d,p) (italics) levels of theory (distances in Å). Reprinted with permission.[16] Copyright 2013, American Chemical Society.

Simplified mechanism of the rearrangements of secondary alkyl cations, presented in Scheme 1b, includes subsequent 1,2-alkyl and 1,2-hydride shifts with intermediate formation of the "opened" cationic structures. With regard to rearrangements of tertiary alkyl cations, similar reaction pathways have their place since the 1960s,[19] but towards secondary alkyl cations this mechanism was substantially modified by Brouwer and Hogeveen in 1972,[20] and by Shubkin *et al*. towards α-olefin oligomerization in 1980.[21] Based on previous studies of pent-2-yl cation rearrangement by Kramer,[22] they proposed involvement of the protonated cyclopropyl intermediates (Scheme 1d) to the process as the only way to explain a great diversity of α-olefin isomerization and oligomerization products.

In 1996, Corma and coll. performed a theoretical study of the rearrangements of pent-2-yl cation using DFT and *ab Initio* methods.[23] In some cases, local energy minima were found for primary carbenium ion Et(Me)CHCH_2^+ (**F** in Figure 3), but the difference between the energies of **F** and pent-2-yl cation amounted to 24–25 kcal·mol^{-1}. At MP2/BLYP and MP2/BP86 levels of theory, cation **F** was not localized. Simulations showed that preferred isomerization proceeds through the edge-protonated cyclopropane ring (**B** in Figure 3) with relatively low energy barrier (<10 kcal·mol^{-1}).

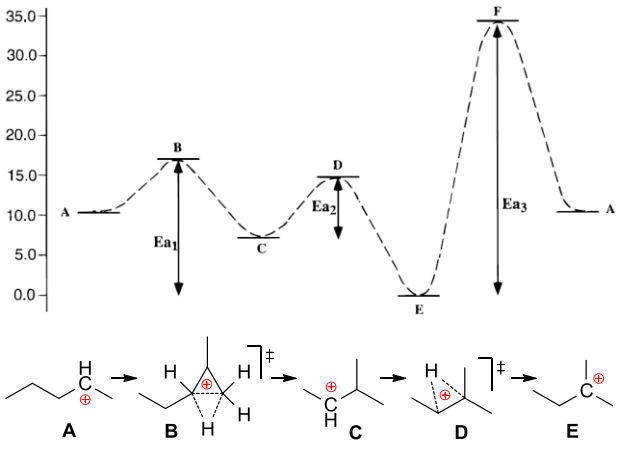
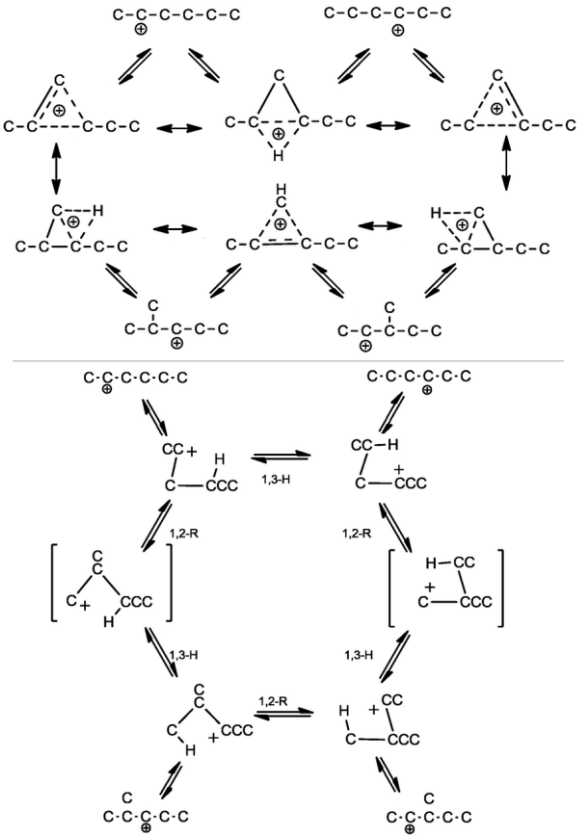


Figure 3 Energy profile corresponding to the branching isomerization of the pent-2-yl cation relative to the energy of tertiary cation. Reprinted with permission,[23] Copyright 1996, American Chemical Society.

In 2016, East and coll. noted that protonated cyclopropane structures in carbocation rearrangement continue to confound. They presented the results of comprehensive study of the rearrangements of alkyl cations

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that addressed all possible reaction pathways.[24] In this work, it was proposed to give up the concept of protonated cyclopropane as an intermediate in rearrangements of carbenium ions, the mechanism of Brouwer and Hogeveen[20] was considered as "incorrect" (Scheme 3).



Scheme 3 Portion of the incorrect Brouwer–Hogeveen alkyl ion rearrangement mechanism[20] (top) and the updated version (bottom).[24] Two of the six closed (meso-PCP+) structures in the updated mechanism are closed-primary ions (shown in square brackets). Reprinted with permission.[24] Copyright 2016, American Chemical Society.

In our view, there is no need to dramatize the situation, much less to pin a labels. A five-minute optimization of protonated cyclopropanes (Figure 4a) revealed a preference of the structure that is close to proposed by East and coll.[24] However, non-contradictory mechanism of the rearrangements of secondary hexyl cations, visualized using PRIRODA program (see Section S3) includes protonated cyclopropane as a transition state with relatively low $\Delta G^{\neq}$ value (Figure 4b). Similar mechanism was proposed previously for this process,[25] without determination of the $\Delta G^{\neq}$.

This model seems to contradict the results of earlier works of Rey *et al.*,[26,27] who proposed isomerization involving a 1,3-hydride shift between secondary and tertiary carbenium ions. This study contains well-balanced conclusion that it is impossible to choose the preferred reaction route. However, as applied to zeolite-catalyzed process, DFT modeling at different temperatures revealed a preference of the alternative mechanism II (Figure 5).

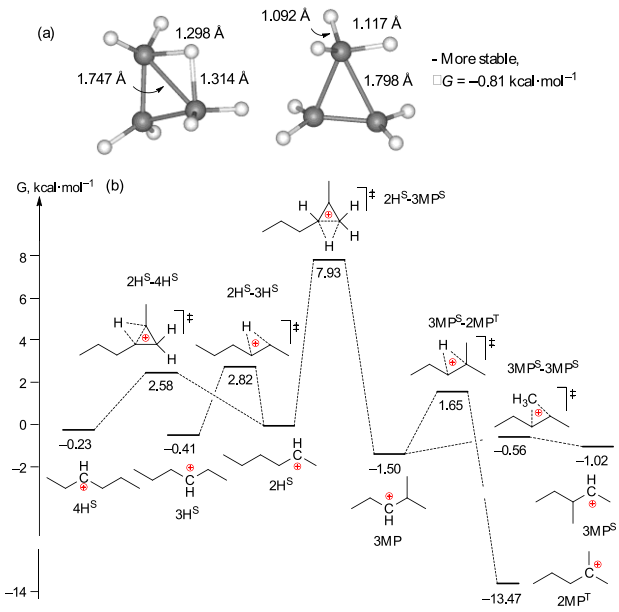


Figure 4 Optimized structures of isomeric protonated cyclopropanes (a) and results of DFT modeling of the rearrangements of secondary hexyl cations (b) (PRIRODA-06, T = 298.15 K, gas phase, PBE functional, 3ζ basis set).

In this way, it is still difficult to make an unambiguous choice between mechanisms of the rearrangements of secondary carbenium ions. Primary carbenium ions are obviously not involved in this process as an intermediates, except when they form a complex with electron donor centers of the catalyst, but that is another story.

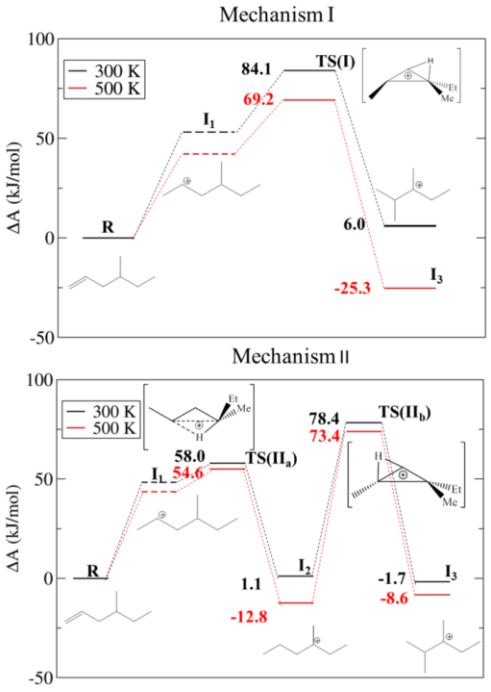


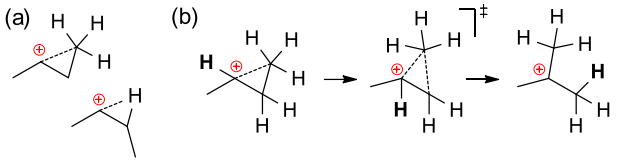
Figure 5 Overall free-energy profiles for mechanisms I and II at 300 and 500 K. A qualitative estimate of the free energy of secondary cation I1 is indicated by a dashed line. Reprinted with permission.[26] Copyright 2019, American Chemical Society.

Butene → Isobutylene rearrangements

It has long been known that butane does not isomerize at an observable rate to isobutane under conditions where *n*-

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pentane and *n*-hexane are rapidly converted into branched isomers.[23] In early works,[28,29] the structure of but-2-yl cation and the mechanism of its rearrangement to $^{t}Bu^{+}$ were studied. Comparison of the alternative modes of stabilization of but-2-yl cation (Scheme 4a) was made using various functional and basis sets,[28] the preference of H-bridged structure was demonstrated in this work.



Scheme 4 Different modes of intramolecular stabilization of but-2-yl cation (a),[28] and mechanism of the rearrangement of but-2-yl cation to $^{t}Bu^{+}$ (b).[29]

A complete set of the possible structures of $C_4H_9^+$ was optimized by Koch and coll.,[29] their study confirmed higher stability of H-bridged structure, but the preference in energy was only 0.4 kcal·mol^{-1}. In this work, the activation barrier of but-2-yl cation to $^{t}Bu^{+}$ rearrangement (Scheme 4b) was calculated to be 19.6 kcal·mol^{-1}.

It should be also noted that in 1990s-2000s in a number of works [30–34] arguments for bimolecular mechanism of butene isomerization were presented. The main experimental proof of bimolecular mechanism is a formation of propylene. In 2023,[35] Studt and coll. carried out DFT modeling of but-2-ene isomerization on H-SSZ-13 zeolite. The results of the modeling (Figure 6) showed the preference of monomolecular reaction pathway, next year the main finding of this work were confirmed for $HAl_{23}MgO_{96}P_{24}$ model catalys.[36]

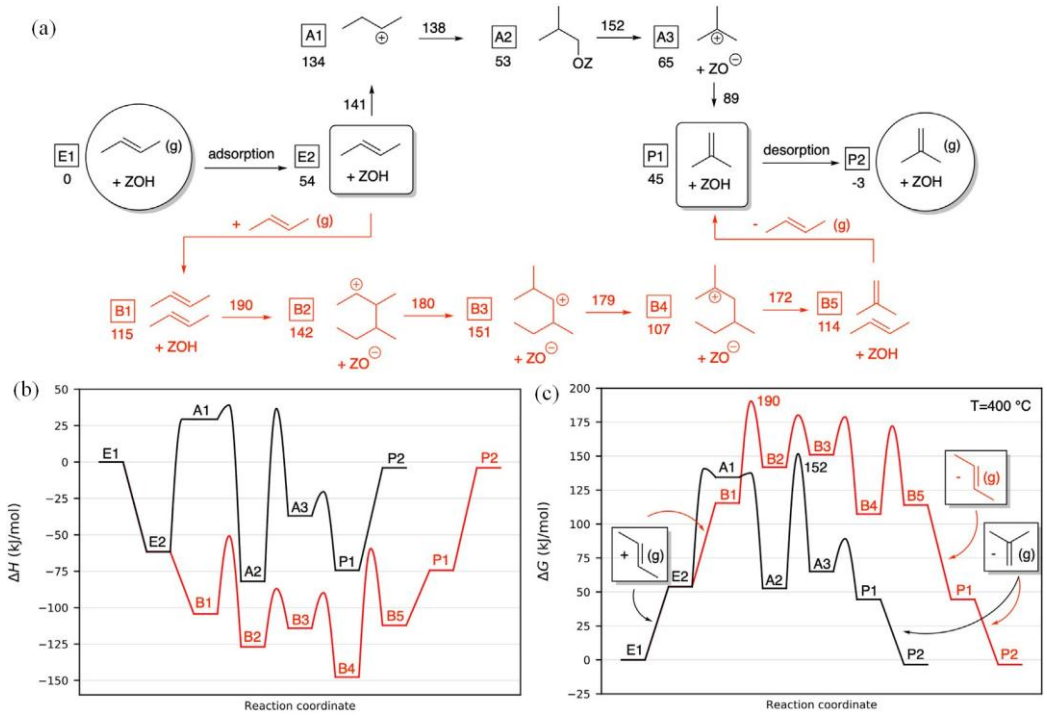


Figure 6 Overview of the monomolecular (black) and bimolecular (red) but-2-ene isomerization mechanisms, referenced to the empty H-SSZ-13 zeolite and but-2-ene in the gas phase. Free energies (T = 400 °C) of intermediate structures are shown next to the structures; free energies of the transition state structures are above the reaction arrows (a). ΔH (b) and ΔG (c) diagrams of the monomolecular and bimolecular but-2-ene isomerization mechanisms. Reproduced with permission, CC-BY 4.0 License (Frontiers).[35] Copyright 2023, the Authors.

It is noteworthy that the geometry parameters of the zeolite pores directly affect the process selectivity: even in 1997 it was shown that the most suitable materials are the catalysts with a pore diameter of 4–5.5 Å (10-membered ring molecular sieves). These materials allow an IB diffusion but they suppress the formation of dimers (and oligomers) which are intermediates leading to by-products.[37] Important finding of this study was the explanation of the formation of propylene and 2-methylbut-2-ene in the frameworks of monomolecular mechanism, by successive methyl transfer involving acidic sites at zeolite surface (Figure 7). High activation barrier of this process (>50 kcal·mol^{-1}) is not insurmountable at high temperatures, and side product formation may happen more easily through one or the other of the mechanisms, depending on the reaction conditions.

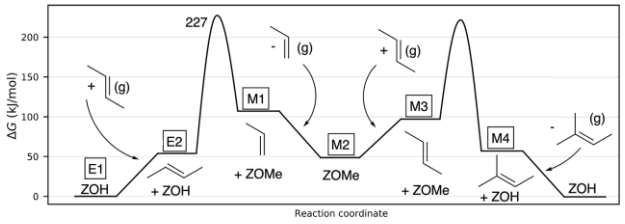


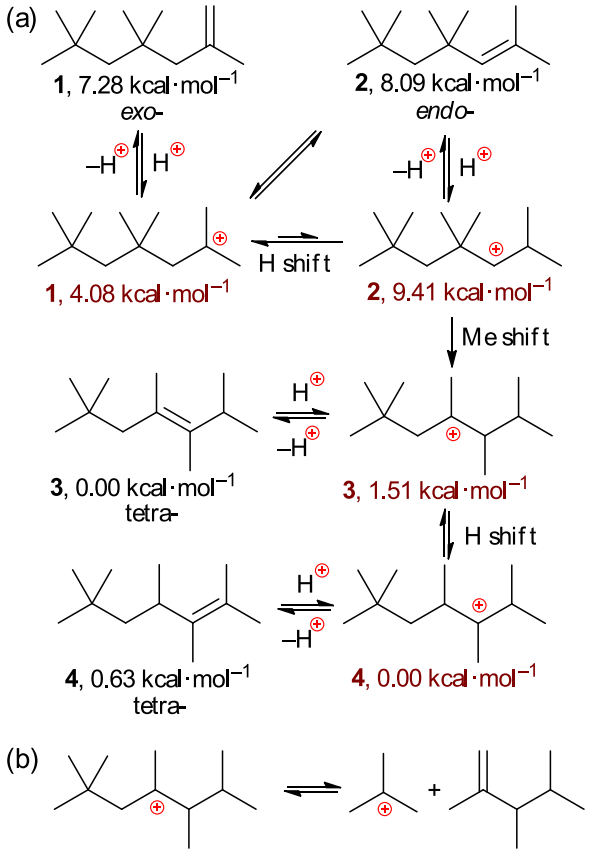
Figure 7 Free energy diagram of the formation of propene from 2-butene and successive methyl transfer (MT) to form 2-methylbut-2-ene (T = 400°C). Reproduced with permission, CC-BY 4.0 License (Frontiers).[35] Copyright 2023, the Authors.

Rearrangements during cationic oligomerization of isobutylene

Cationic oligomerization of IB in non-polar reaction medium, initiated by strong Brønsted or Lewis acids, or *in situ* generated carbenium ions, is a barrierless process that

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proceeds below –100 °C.[4,38] When the temperature rises, IB oligomerization is complicated by proton transfer and rearrangements of carbenium ions. DFT modeling of polyisobutylene (PIB) formation in the frameworks of conventional mechanism of isomerization *via* 1,2-H and 1,2-Me shifts (B3LYP, 6-31G level of theory) revealed the relative stability of the corresponding cations (Scheme 5a).[39] Even though tertiary cation **4** is the most stable intermediate, its formation requires a transition through unstable cation **2**. It was unexpectedly found that *exo*-olefin is more stable in comparison with *endo*-isomer, i.e. the formation of *exo*-olefinic group is favorable both sterically (not surprisingly) and thermodynamically. The latter deserves special attention due to a formal contradiction to Zaitsev's rule. It might be worth mentioning this fact during the study of the topic "relative stability of substituted olefins", at least as a note. Another process accompanying cationic oligomerization of IB is a chain scission (Scheme 5b).[39,40]



Scheme 5 Interconversions and relative stability (*E* scale) of olefins (black) and model cations (red) based on isobutylene trimer (a)[39] and proposed mechanism of the chain scission (b).[39]

In addition, IB oligomers with internal >C=CH_2 fragment can be detected in ^{1}H NMR spectra (Figure 8).[4]

The formation of similar fragments was explained by 1,3-methide shifts (Scheme 6).[41]

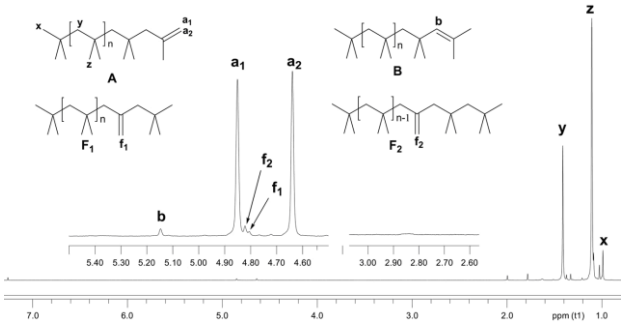
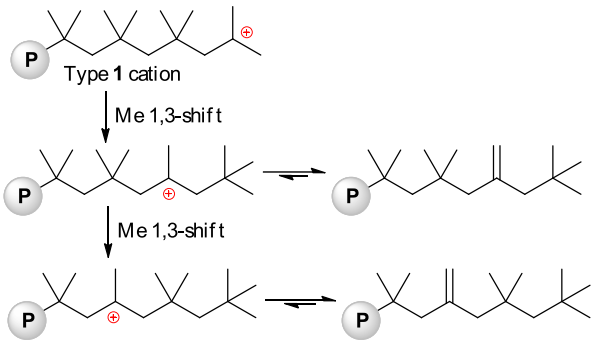


Figure 8 ^{1}H NMR spectrum of PIB obtained with $AlCl_3/OBu_2/H_2O$ initiating system.[4]



Scheme 6 Formation of internal *exo*-olefins during cationic polymerization of isobutylene.[41]

All of the above seem scientific and gives an impression of the amazing diversity of cationic rearrangements proceeding in different *competing* pathways. However, one notable experimental fact, the structure of the *vinylidene* isomer of isobutylene trimer (Figure 9a, typical NMR spectrum is presented in Figure S2), spoils the whole point. This structure regularly appears as a reaction product in works on IB oligomerization,[42,43] but its formation is usually explained in terms of "alkylation" or "rearrangement" without specifics. Above-mentioned "1,3-methide shift" [41] represents more the exception than the rule in trying to give a science feel to mechanistic interpretation of this reaction. Furthermore, despite their practical importance and apparent simplicity, the reaction presented in Figure 9a did not get into organic chemistry textbooks.

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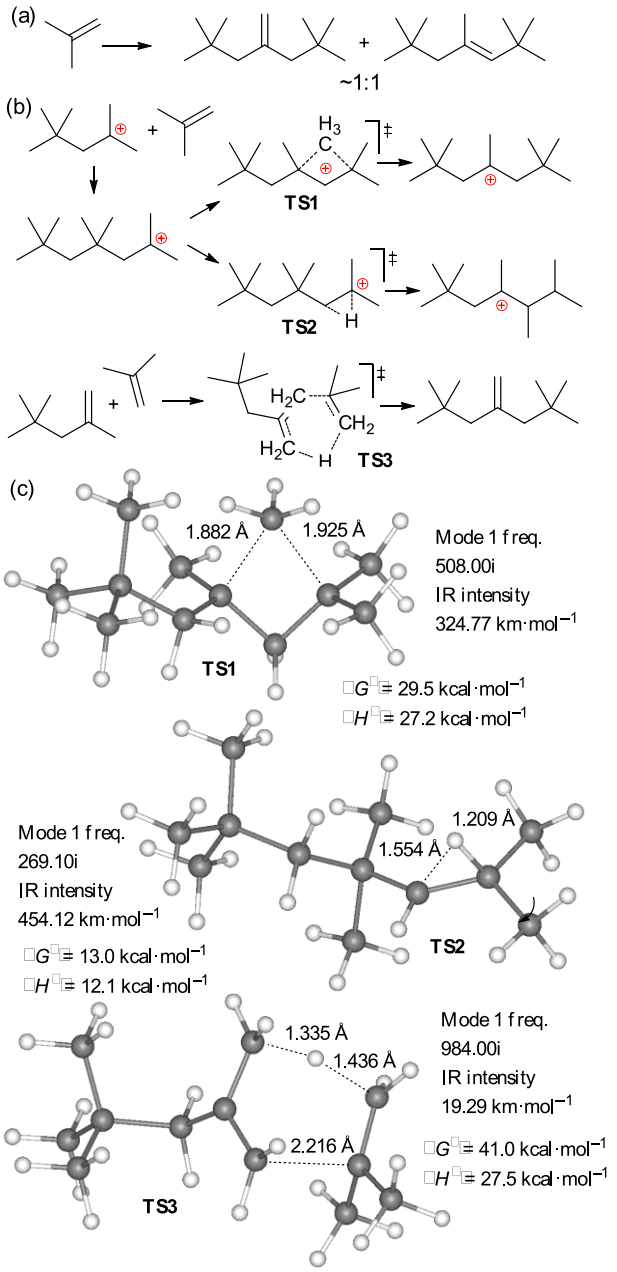


Figure 9 The products of IB trimerization (a),[42] possible reaction pathways for the reaction of IB dimer with IB (b), calculated geometries and relative free energies of the corresponding transition states (c, this work).

To date, comparative DFT modeling of IB trimerization *via* 1,3-Me shift among other processes (Figure 9b) was not performed. Here we have taken the liberty to fill the gap using PRIRODA program. Calculated $\Delta G^{\neq}$ value for TS1 amounted to 29.5 kcal·mol^{-1}. The $\Delta G^{\neq}$ for TS2 (1,2-H shift followed by immediate barrierless 1,2-Me shift) was 13 kcal·mol^{-1}. The activation barrier for thermally induced reaction of *exo*-isomer of IB dimer with IB *via* six-membered TS3 was 41 kcal·mol^{-1} in G scale. Surprisingly, the $\Delta H^{\neq}$ values for 1,3-Me shift in carbenium ion *via* TS1 and thermally induced reaction *via* TS3 were close to each other, ~27 kcal·mol^{-1}. Obviously, these intramolecular and bimolecular processes should not be compared directly, but the mere fact is remarkable. And in any case, simple DFT modeling of isomerization of $^{t}BuCH_2CMe_2CH_2CMe_2^+$ does not answer the question of the formation of IB trimer, casting doubt on the formation of this cationic intermediate.

The actual mechanistic studies of IB oligomerizaion are mainly addressed to the revealing of the factors affecting the content of vinylidene end-groups and chain release, in view of the synthesis of highly reactive PIBs that hold the major share of the PIB market (more than 70%).[44] These investigations are not of interest in the context of the present work as they are mainly aimed at initiation [45] and chain release [4] *via* proton transfer involving Lewis base components of the catalysts. However, the results of our recent theoretical study are of interest considering that BF_3/MeOH catalyst can initiate IB oligomerization by concerted mechanism, with a formation of $Me_3CCH_2CMe_2^+$ species, bypassing the stage of $^{t}Bu^+$ formation.[46]

Rearrangements and fragmentations of paraffins during catalytic hydrocracking – and *vice versa*

Acid-catalyzed rearrangements and fragmentations of paraffins evidently proceed *via* intermediate formation of carbenium ions and olefins. This process was studied in many experimental works, the mechanism of isomerization of paraffins is actually a mechanism of isomerization of carbenium ions discussed above. However, acid-catalyzed hydrocracking in certain implementations represents a fragmentation of broad hydrocarbon fractions, which is one of the most important methods of industrial production of propylene.[47] This widely implemented process was successfully optimized decades earlier without the use of DFT modeling. The development of the catalysts of this process continues, and the importance of quantum-chemical simulations of similar reactions is growing.[48] For example, acid-catalyzed fragmentation of higher α-olefins was the subject of recent study of Wang and coll.[49] (Figure 10).

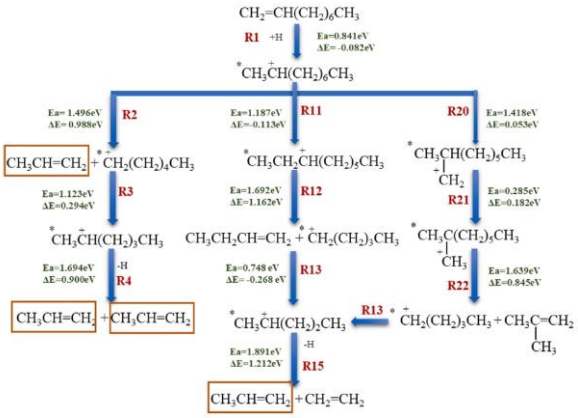


Figure 10 Acid-catalyzed fragmentation of non-1-ene with a formation of propylene and other low-MW hydrocarbons. Reproduced with permission.[49] Copyright 2021, Elsevier. 1 eV = 23 kcal·mol^{-1}.

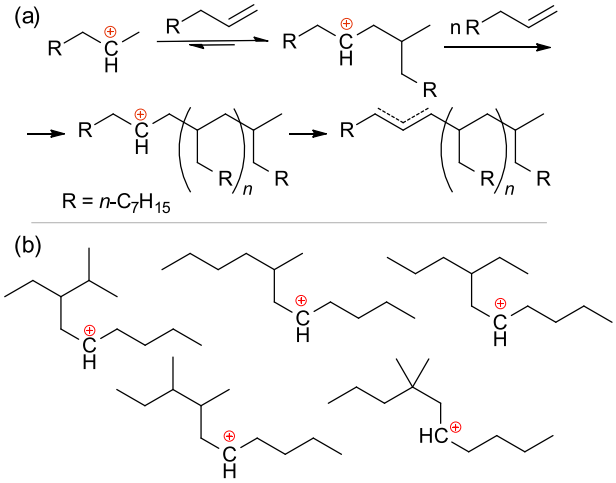
Activation barriers of fragmentation turned out to be higher than activation barriers of isomerization. The reverse process, oligomerization of light olefins with a formation of high-boiling hydrocarbons, is of great practical importance. However, this process proceeds with high rate when methylenealkanes are used as a substrates.[50] In recent review,[51] the use of metal-doped zeolites and related acidic phases was discussed in detail.

Rearrangements during cationic oligomerization of dec-1-ene and other higher olefins

Oligomerization of higher α-olefins, in particular dec-1-ene, is the basis of industrial production of poly-α-olefin (Group IV) motor oils and lubricants.[5] Despite pioneering

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work of Shubkin,[21] by the end of 1990s the structure of dec-1-ene oligomers was often regarded as a result of subsequent additions of dec-2-enyl cation to dec-1-ene, and so on (Scheme 7a).[52,53] In the frameworks of this mechanism, dec-1-ene oligomers should contain only long C_8 branches and single methyl branch. After hydrogenation, structurally uniform oligomers should be formed – however, the real picture is more downbeat, considering isomerization of starting olefin, as was shown in Scheme 3. Already on the example of hex-1-ene dimerization it is clear that at least five $C_{12}H_{25}^+$ intermediates can be formed (scheme 7b), and each of them in turn is able to isomerization. Structurally uniform dec-1-ene oligomers can be obtained only using coordination oligomerization,[54] and remarkably, high activity and structural homogeneity of the oligomers were achieved just recently.[55–58]



Scheme 7 Simplified but overly idealized mechanism of cationic oligomerization of dec-1-ene (a).[53] Possible structures of initially formed hex-1-ene dimers (b).

Real products of cationic dec-1-ene oligomerization, including valuable C30 and C40 fractions, represent complex mixtures of many tens of compounds containing long- and short-chain branches, >C=CH–, –CH=CH– and >C=CH_2 chain-end fragments.[59–65] The exceptional complexity of the oligomerization products can be illustrated by typical GC trace of hydrogenated dec-1-ene dimer (Figure 11).[66]

In this work, the mechanism of the formation of isomers was kept to a sequence of 1,2-H shifts in starting decen-2-yl cation, followed by addition of different secondary carbenium ions to dec-1-ene molecule. Similar reaction sequences are unable to explain the observed diversity of the reaction products. Evidently, protonated cyclopropyl intermediates [20] or East cations [24] are also accounted for, in view of theoretical studies of rearrangements of carbenium ions. Theoretical simulations of cationic dec-1-ene dimerization *via* protonated cyclopropane intermediates revealed 45 isomeric products.[67] Attempts were made to predict the degree of branching depending on the structure of the starting olefin (for example, similar studies were performed for isomeric octenes[68]). The value of this kind of study seems doubtful due to the ease of isomerization of starting olefins *via* 1,2-H shifts.

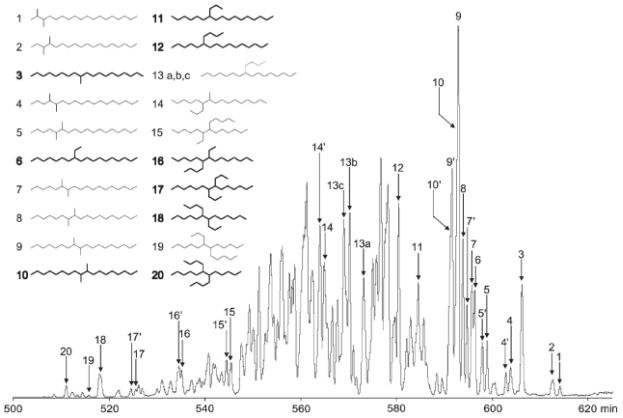


Figure 11 Typical gas chromatogram and the structures of $C_{20}H_{42}$ isomers determined using MS data. The bold numbers and structures indicate isomers formed *via* acid-catalyzed isomerisation of dec-1-ene before dimerization, couples of diastereomers are marked as X and X′. Reproduced with permission.[66] Copyright 2011, John Wiley & Sons, Ltd.

Overall, theoretical studies of cationic oligomerization of dec-1-ene and other linear α-olefins are fragmentary. In a number of works, the stage of initiation attracted the attention of researchers,[69] often through the use of short-chain olefins as a model compounds. For example, activation barrier for hex-1-ene protonation in reaction with $AlCl_3 \cdot H_2O$ (B3LYP-D3/Def2TZVPP level of theory, IEFPCM solvent model) was estimated by the value of 21 kcal·mol^{-1}.[70]

The chemistry of carbocations in higher school

As mentioned above, traditional organic chemistry courses at undergraduate level do not provide for deeper understanding of the mechanisms of cationic rearrangements and oligomerization of olefins. From a methodological perspective, simplified reaction mechanisms (Schemes 1 and 7) are accessible to a general student audience. Moreover, similar simplified schemes integrate the material and reinforce basic knowledge (e.g., a range of stability of carbenium ions). But there is a downside: a distorted idea of the chemistry of carbenium ions lead to idealization of the composition and properties of real raw materials and products of modern petroleum industry. A "golden middle" towards the knowledge should be achieved, and simple DFT modeling with corresponding visualization can significantly help to solve this methodological task.

Let us repeat, this focus article not just discusses mechanistic aspects of the cationic transformations of olefins, we also have permitted ourselves to present here some results of simple and fast DFT modeling. After appropriate additional treatment in terms of visualization, these results may prove helpful in the study of organic chemistry in higher school. The above-mentioned PRIRODA program [12] is so undemanding to resources, that it works on any PC, and can solve simple mechanistic tasks literally in minutes.‡ And whether it is time to use similar 'fast' DFT modeling as routinely available tool to solve any scientific or methodological problems of the chemistry of molecules, and to teach anyone who is willing to learn?

Conclusions and outlook

‡ However, there is nothing stopping the use of ORCA, GAUSSIAN or other appropriate program.

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In this feature article, we briefly examined various issues related to formation and rearrangements of carbocations in alkane and alkene chemistry. The results of both experimental and theoretical studies clearly demonstrate that the reaction mechanisms of many industrially relevant processes of modern petroleum chemistry are not confined to 1,2-H and 1,2-alkyl shift sequences. Understanding of the possibility of the formation of cyclic carbocations expands the understanding of molecular transformations in general. This is probably the main benefit of this concept for teaching and understanding chemistry as a science of matter transformations.

At the same time, the work on this content allowed to reveal interesting and promising problems in understanding of the cationic reactions of paraffins and olefins. DFT modeling of the reactions of carbocations as such are of theoretical and methodological interest and, with one exception (above-mentioned IB trimerization) everything is more or less clear. At the level of concepts and for illustrative purposes, DFT modeling in gas phase at low level of theory seems acceptable and sufficient.

However, the solving of real scientific tasks on the development of the processes of modern petrochemical industry require the use of more complicated and demanding methods of quantum chemical modeling (the search of the most appropriate functional and basis, solvent corrections, consideration of the conformation distribution etc).[71] Below we tried to outline the actual problems for which high-level DFT modeling may prove useful.

– Butane (butene) → isobutane (IB) isomerization that is characterized by high activation barriers and mechanistic ambidity for "naked" but-2-yl cation,[28,29] is quite feasible even for 2-methylprop-1-yl cationic intermediate, when it is associated with a catalyst species or surface. However, in the latter case DFT modeling of the process requires the development of the correct surface models, which is being done in recent years. [35,36,72–74]

– $AlCl_3$ is still the most available catalyst for cationic oligomerization of α-olefins with a formation of medium-viscosity oil basestocks.[75] However, this process is accompanied by the formation of chloroalkanes. This experimental fact, which has become a particular problem in production of polyolefin oils, is weakly reflected in scientific periodicals; theoretical analysis of this side process with the involvement of DFT modeling would not be amiss.

– The use of ionic liquids as a catalytic phases for IB and α-olefin oligomerization is in trend,[40,76,77] but quantum-chemical modeling of similar processes is still limited to calculations of starting complexes and reactions of isolated ion pairs.[40] More comprehensive theoretical analysis is clearly required.

– Acid-catalyzed paraffin hydrocrackind and reverse processes remain in need for thorough theoretical analysis, including development of the catalyst surface models mentioned above.

Simplification of the calculation methods is appropriate for the creation of the concept and no doubt for educational objectives. At the same time, real modeling of the industrially relevant processes requires the development and use of state-of-the-art theoretical approaches.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.8209.

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