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Propane transformations on aluminum chloride—cobalt chloride clusters: a quantum chemical study

I. P. Gloriozov, G. M. Zhidomirov, and M. I. Shilina★

Department of Chemistry, M. V. Lomonosov Moscow State University,
1 Leninskie Gory, 119991 Moscow, Russian Federation.
Fax: +7 (495) 932 8846. E-mail: mish@kinet.chem.msu.ru

Density functional PBE/TZ2p quantum chemical calculations of activated complexes and pathways of model catalytic transformations of propane under the action of aluminum chloride—cobalt chloride ionic bimetallic complexes were carried out. The formation of an intermediate with a broken C—C bond can occur on the cationic cluster $CoAlCl_4^+$ characterized by the strongest coordination of propane molecule. The activation barrier to the reaction is $\Delta G = 25.0$ kcal mol^{-1}. Activation of alkane C—H bonds follows the alkyl pathway involving the formation of bimetallic alkyl complexes. The interaction of activated hydrocarbon fragments bound to transition metal atoms in cobalt-chloroaluminate clusters can result in alkane metathesis products (in this case, ethane and a polymetallic cluster containing an extended-chain alkyl radical).

Key words: quantum chemical calculations, density functional theory, PBE/TZ2p method, alkane activation, ionic complexes, bimetallic alkyl complex, aluminum chloride, cobalt chloride, propane, transition state.

Catalytic systems based on aluminum halides and transition metal salts are efficient in the isomerization of alkanes, alkylation of unsaturated and aromatic compounds, and cracking of heavy paraffins.[1—4] Transformations of alkanes in the presence of Lewis acids are usually treated from the standpoint of the carbocation mechanism.[5] As a rule, the promoting action of transition metal salts on the catalytic activity of Lewis acids is explained by the formation of more acidic complexes.[1,2,6]

At the same time, transition metal cations can directly react with hydrocarbons upon, *e.g.*, the introduction into zeolites. In this case, the mechanism of hydrocarbon activation may involve the formation of alkylmetal compounds as intermediates. Indeed, such intermediates were detected by spectroscopic methods in the reactions of alkanes with the Zn-, Ga-, and Co-modified zeolites,[7—9] as well as observed in the gas-phase reactions of alkanes with metal ions (Co^+, Fe^+, Ni^+, Mo^+).[10—13]

The involvement of transition metal cations in the activation of alkanes is, in particular, evidenced by the composition of low-temperature (150—220 K) conversion products of C_7—C_{10} paraffins, which was first performed on aluminum halide complexes with various promoters.[14] It was found that low-temperature transformations of alkanes follow two pathways depending on the nature of promoter (alkyl chloride or transition metal halide). Reactions under the action of aluminum halide—transition metal halide bimetallic complexes result in isoalkanes and in high yields of *n*-alkanes whose carbon chains are one carbon atom shorter than the initial *n*-alkane chain (such products are not typical of the reactions catalyzed by conventional acidic catalysts).[14] In this case, the content of cracking products is at most 5% (*cf.* 70—80% for the reaction catalyzed by aluminum chloride in both individual form and promoted by organohalogen derivatives).

A similar (to some extent) composition of products was obtained in alkane metathesis on tantalum hydrides immobilized on silica gel.[15] In this case, saturated hydrocarbons are catalytically transformed into heavier and lighter alkanes, while isomerization is a minor process.

Using low-temperature condensation technique and *in situ* spectroscopic methods, it was found[16—17] that the species catalytically active in low-temperature conversion of alkanes are formed at 120—170 K in bimetallic systems in the reactions of the 1 : 1 and 2 : 1 aluminum halide—cobalt halide molecular complexes. According to spectroscopic data and quantum chemical calculations, these are ionic associates (clusters), which simultaneously contain cobalt and aluminum atoms in the cationic and anionic fragments, *viz.*, $[CoCl(AlCl_3)_k]^+$ (**1a**) and $[CoCl_3(AlCl_3)_m]^-$ (**1b**), where $k = 1$—2 and $m = 1$—3 (see Refs 16 and 17).

It was of interest to establish how the species detected can react with alkanes to result in unusual products. One can assume two main pathways of the reactions of ionic complexes **1a**,**b** with alkanes, namely, a carbocation

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pathway involving the formation of the species $H^-[CoCl(AlCl_3)_k]^+$ and $R^+[CoCl_3(AlCl_3)_m]^-$ and an alkyl pathway involving the formation of the species $R^-[CoCl(AlCl_3)_k]^+$ and $H^+[CoCl_3(AlCl_3)_m]^-$.

According to the density functional calculations[18] of the energies of the reactions of aluminum halides and cobalt halides with propane as a model hydrocarbon, the formation of hypothetical intermediates from the initial reactants in the gas phase is energetically favorable:

$$2\,AlCl_3 + 2\,CoCl_2 + C_3H_8 \longrightarrow HCoAlCl_4 + C_3H_7[CoAlCl_6] \quad (1)$$

$(\Delta E = -25.8\ \text{kcal mol}^{-1})$

$$2\,AlCl_3 + 2\,CoCl_2 + C_3H_8 \longrightarrow (1\text{-}C_3H_7)CoAlCl_4 + H[CoAlCl_6] \quad (2)$$

$(\Delta E = -35.6\ \text{kcal mol}^{-1})$

The processes considered are comparable in energy. Abstraction of a proton is more probable than that of the hydride ion. In addition, the possibility of formation of alkyl derivatives in these reactions is suggested by the results of quantum chemical calculations of ternary complexes aluminum halide—cobalt halide—propane.[19] It was found that alkane is coordinated to the transition metal ion rather than to the stronger Lewis center (Al) and that the character of polarization of the saturated C—H bonds changes. If the reaction of aluminum halide with propane causes the negative atomic charge of carbon to decrease and thus favors the formation of carbocations, coordination of bimetallic complexes with alkane produces the opposite effect, *viz.*, an increase in the electron density on the carbon atom. This polarization favors the formation of alkylmetal compounds in which the organyl radical has a carbanionic character.

It is believed[19] that the formation of σ-complexes with an alkane coordinated to the transition metal ion and alkylmetal derivatives may lead to an unusual reaction (atypical of catalysis by Lewis acids), *i.e.*, to alkane metathesis where an *n*-alkane is transformed into another *n*-alkane whose carbon chain is one atom shorter than that of the starting hydrocarbon. The key step of this reaction is the σ-bond metathesis involving intramolecular exchange in the coordination sphere of the metal atom.[15] Under drastic conditions (gas phase), the ions Fe^+, Ni^+, Co^+, Ta^+, and some other can also form metathesis products by activating not only the alkane C—H, but also C—C bonds.[10—13]

The aim of the present work was to establish particular pathways of alkane transformations under the action of bimetallic complexes of aluminum chloride with cobalt chloride. In this connection, we carried out quantum chemical calculations of reactive complexes and pathways of propane transformations under the cation of these bimetallic complexes. We have found the pathways of formation of alkane metathesis products, which in this case involve elimination of ethane molecule and formation of a polymetallic cluster containing a longer-chain alkyl radical.

Calculation Procedure

Earlier,[16—17] we have performed quantum chemical calculations of the structures and vibrational spectra of the molecules $AlCl_3$, Al_2Cl_6, $CoCl_2$, Co_2Cl_4, and their 1 : 1 or 2 : 1 molecular complexes by the density functional methods using the B3LYP (see Ref. 20) and PBE (see Ref. 21) functionals. The results obtained are in reasonable agreement with each other and with experimental data.

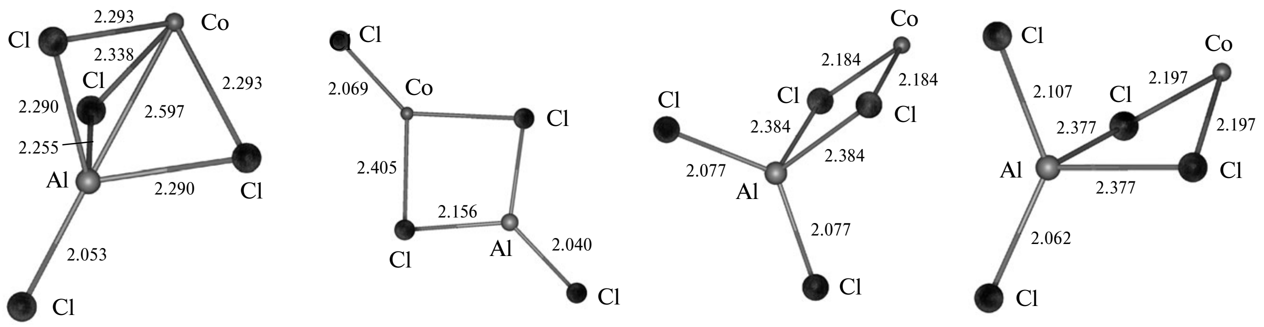
In the present work, we also used the same approach. The geometries of the molecules and transition states studied were optimized for the gas phase conditions within the framework of the density functional theory with the PBE nonempirical nonlocal functional.[21] We used the extended TZ2p basis set of contracted Gaussian functions: (311/1) for the H atoms, (611111/411/11) for the C atoms, (6111111111/611111/11) for the Al and Cl atoms, and (611111111111/51111111/5111) for the Co atoms. We assumed a multiplicity of 4 and 7 for the complexes with one and two Co atoms, respectively. The stationary points located were identified by analyzing the Hessians.

Thermodynamic functions (G) were calculated using statistical relationships for the rigid rotator—harmonic oscillator model and $T = 298.15$ K. The correspondence between the transition states located, starting compounds, and products was checked by the intrinsic reaction coordinate (IRC) method. Atomic charges were calculated according to Hirshfeld.[22] All calculations were performed on an MBC-100k cluster at the Joint Supercomputer Center (Moscow) using the PRIRODA-04 program.[23—24]

Results and Discussion

The structure of the bimetallic cation $CoAlCl_4^+$. Reactions of experimentally detected ionic complexes **1a** and **1b** of the general formula $[CoCl(AlCl_3)_k]^+[CoCl_3(AlCl_3)_m]^-$ with propane were studied taking the simplest complexes $CoAlCl_4^+$ and $CoAlCl_6^-$ as examples. Earlier,[19] calculations performed in the same approximation as that used in the present work have revealed two conformations, **C1** and **C2**, of the cation $CoAlCl_4^+$. We located yet another stable structure **C3** (Fig. 1).

The calculated relative energies and atomic charges of metals in complexes **C1**—**C3** are listed in Table 1. It follows that complex **C3** appears to be the least stable among all calculated structures, the barrier to the conformational transition **C1**→**C3** *via* the transition state **TS1** (see Fig. 1) being 11.1 kcal mol^{-1}. At the same time, in complex **C3** it is the Co atom that bears the largest positive charge. This should favor a more efficient reaction with alkane molecules. Indeed, calculations for propane showed that it is cation **C3** whose complex with propane cor-



C1 **C2** **C3** **TS1**

Fig. 1. Structures **C1**—**C3** of the bimetallic cation $CoAlCl_4^+$ and transition state **TS1** between complexes **C1** and **C3** obtained from PBE/TZ2p density functional calculations. Here and in Figs 2—6, 8, and 9 the bond lengths are given in Å.

responds to the alkane conversion point on the reaction coordinate.

Coordination of propane molecule on the cationic cluster $CoAlCl_4^+$. As shown earlier,[19] the strongest complexes of propane with the bimetallic cation $CoAlCl_4^+$ are formed if the methyl and methylene groups are coordinated to the Co atom in structure **C1**; the corresponding stabilization energies are 25—27 kcal mol^{-1}. We found some other conformations of the propane complexes with cations **C1** (complexes **2a**—**c**) and **C3** (complexes **2d**,**e**) with close energies (Fig. 2). In all complexes, the interaction of the cobalt atom with the alkane molecule involves at least two carbon atoms. In complexes **2b**,**c**, propane is mainly coordinated by the methylene (**2b**) and methyl (**2c**) groups, complex **2c** being similar to complex **2b** shown in Fig. 2. The interatomic distances Co—C in complex **2c** are 2.275 and 2.421 Å for the primary and secondary carbon atoms, respectively. In complex **2b**, the bond between the Co atom and the secondary C atom is the shortest (2.196 Å). Unlike complexes **2b**,**c**, in structure **2a** all three carbon atoms are involved in the interaction with cation **C1** and the bond between the Co atom and the secondary C atom elongates to 2.243 Å. A structure with three carbon atoms similar to complex **2a** was located when studying the reaction of propane with cation **C3** (complex **2e**). In this case, methyl groups make a greater contribution to the interaction with the cobalt atom, as indicated by a decrease in the bond length *d*(Co—C) between Co and Me groups and simultaneous increase in the bond length *d*(Co—C) between Co and CH_2 group (see Fig. 2). As a result, these bond lengths in structure **2e** differ by 0.05 Å (*cf.* 0.25 Å in structure **2a**). In structure **2d**, only methyl groups are involved in the interaction of propane with cation **C3**. It is of note that the most stable theoretical model, *viz.*, the complex of propane with the isolated Co^+ cation ($Co^+C_3H_8$) (see Fig. 2) is structurally similar to complex **2d**.

Table 1. The total (*E*) and relative (ΔE and ΔG) energies and atomic charges (*q*) of Co and Al in structures **C1**—**C3** of bimetallic cation $CoAlCl_4^+$ calculated by the PBE/TZ2p method

Structures	$-E$/a.u.	ΔE	ΔG	*q*(Co)	*q*(Al)
		kcal mol^{-1}		a.u.	
C1	3465.023362	0	0	0.509	0.448
C2	3465.019159	2.6	1.5	0.309	0.612
C3	3465.008181	9.5	8.1	0.602	0.424

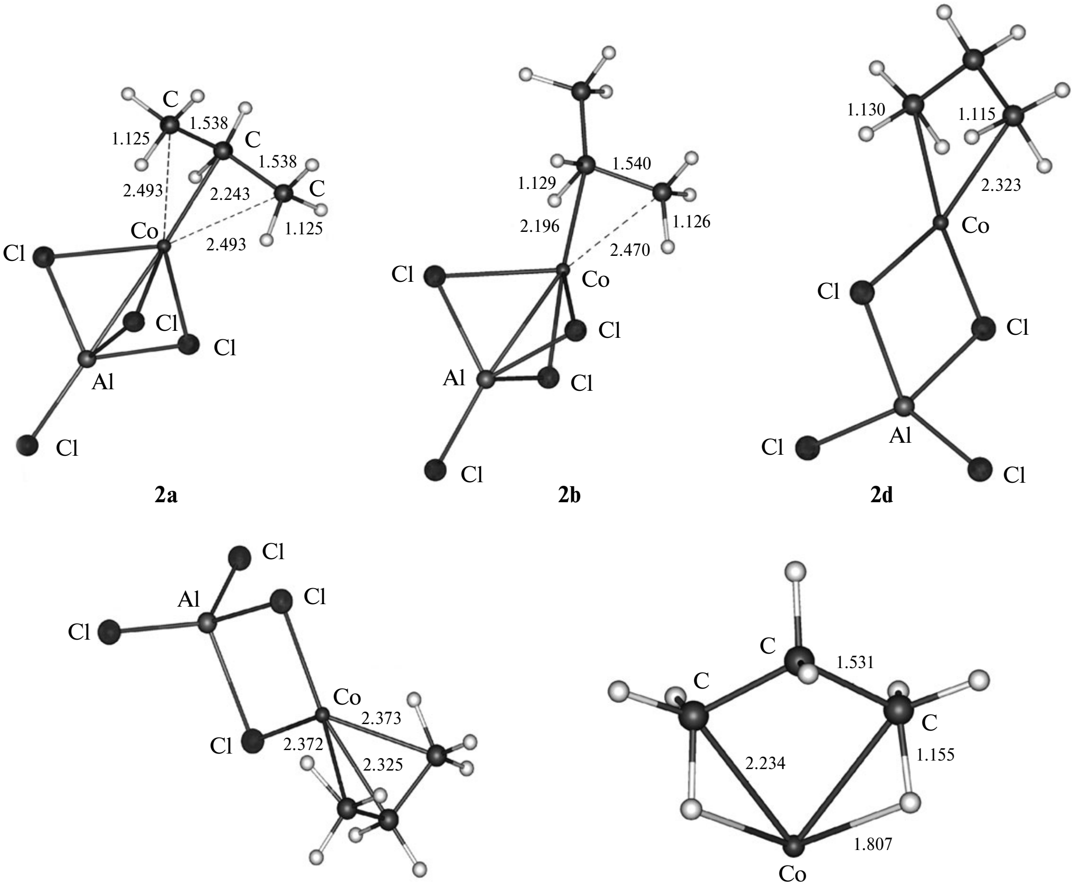
The calculated relative energies (ΔE) of formation of associates $C_3H_8 \cdot CoAlCl_4^+$ (**2a**—**e**) and the charges (*q*) on the Co atoms and atoms of the propane molecule in the complexes are listed in Table 2. The calculated stabilization energies of the propane complexes with bimetallic cations **C1** and **C3** are close to the calculated[25] (29.3 kcal mol^{-1}) and experimental[26] (30.8 kcal mol^{-1}) values for the complexes with the isolated cobalt ions $Co^+C_3H_8$.

A comparison of the data in Tables 1 and 2 shows that, although the difference in the relative ΔG values for free cations **C1** and **C3** is large (~8 kcal mol^{-1}), the propane complexes with cations **C1** and **C3** (complexes **2a**—**c** and **2d**,**e**, respectively) have much closer energies ($\Delta G <$ < 4 kcal mol^{-1}). Thus, the propane molecule can be coordinated to the cation $CoAlCl_4^+$ in all structures shown in Fig. 2.

Also, from the data in Table 2 it follows a considerable increase in the positive atomic charge of Co and in the

Table 2. The total (*E*) and relative (ΔE and ΔG) energies of the complexes of propane with the bimetallic cations **C1** (srtuctures **2a**—**c**) and **C3** (structures **2d**,**e**) and with isolated Co^+ cation and the charges (*q*) on the Co atom and on the atoms of propane molecule in the complexes

Complexes	$-E$/a.u.	ΔE	ΔG	*q*(Co)	*q*(C_3H_8)
		kcal mol^{-1}		a.u.	
2a	3584.073877	0	0	0.253	0.495
2b	3584.071748	1.3	0.3	0.267	0.460
2c	3584.070955	1.8	1.0	0.283	0.433
2d	3584.067140	4.2	2.6	0.321	0.537
2e	3584.064999	5.6	3.7	0.318	0.555
$Co^+(C_3H_8)$	1501.300740	—	—	0.472	0.528



2a **2b** **2d**

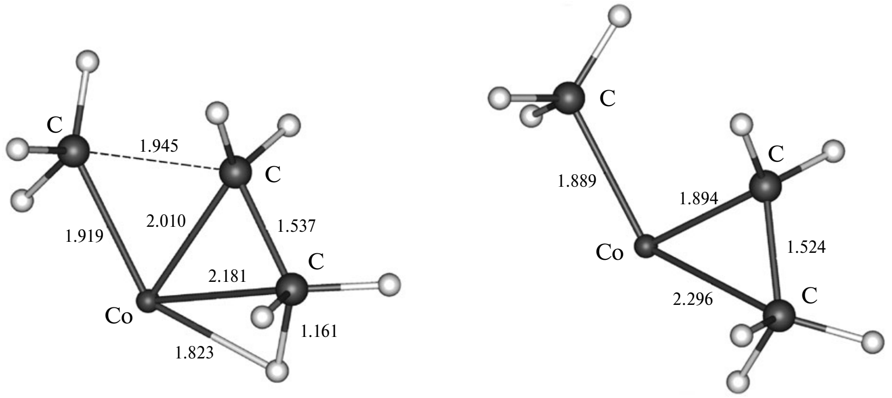
2e $Co^+C_3H_8$

Fig. 2. Structures of the complexes of propane with bimetallic cations **C1** (complexes **2a**,**b**) and **C3** (complexes **2d**,**e**), and the structure of the model complex of propane with isolated cobalt cation ($Co^+C_3H_8$) calculated by the PBE/TZ2p method.

total charge on the propane molecule in compounds **2a**—**e** on going from the complexes with cation **C1** to the complexes with cation **C3**. As a result, the charges *q*(Co) and $q(C_3H_8)$ in the structures **2d** and **2e** approach the corresponding values in the model complex $Co^+C_3H_8$ (see Table 2). In this connection, one can expect that the pathways of further transformations of alkanes under the action of bimetallic ionic clusters of aluminum chloride with cobalt chloride may appear to be close to those observed for isolated ions including the case of oxidative addition at the C—C bond.

Oxidative addition at the C—C bond. Oxidative addition is assumed to be a key step of gas-phase alkane reactions under the action of Co^+ ions resulting in activation products of not only C—H, but also C—C bonds in hydrocarbons.[10—13] Our calculations of the C—C bond activation in propane showed (Fig. 3) that the energy barrier to transformations of the model complex $Co^+C_3H_8$ *via* transition state **TS2** is 15.3 kcal mol^{-1}, while the relative energy of the intermediate ($CH_3CoC_2H_5^+$) is 4.8 kcal mol^{-1} higher than that of the starting complex. These results agree with those of the B3LYP calculations[27] of ethane activation by cobalt cations (the energy barrier to the reaction is 21 kcal mol^{-1} and the relative energy of the intermediate ($CH_3CoCH_3^+$) is 14 kcal mol^{-1} higher than that of the starting complex). Similar activation barriers to oxidative addition at the C—C bond in ethane or propane were obtained in guided ion beam mass spectrometry studies of reactions of Co^+ ions.[26,28]

According to our calculations, not only isolated cations, but also bimetallic ionic complexes $CoAlCl_4^+$ can activate alkane C—C bonds with moderately high activation barriers. In the case of the bimetallic cluster $C_3H_8 \cdot CoAlCl_4^+$, we located the transition state **TS3** of oxidative addition of propane at the C—C bond, which lies on the pathway from complex **2d** to intermediate **IM1**. The activation barrier is 25 kcal mol^{-1}. The structures located are shown in Fig. 4. The energy of intermediate **IM1** is 22.2 kcal mol^{-1} higher than that of complex **2d**, which suggests a transient type of the structure **IM1**. A possible route of subsequent transformations of this intermediate is the addition of hydrogen atom to the alkyl



TS2
$\Delta E = 15.4$; $\Delta G = 15.3$

$CH_3CoC_2H_5^+$
$\Delta E = 6.9$; $\Delta G = 4.8$

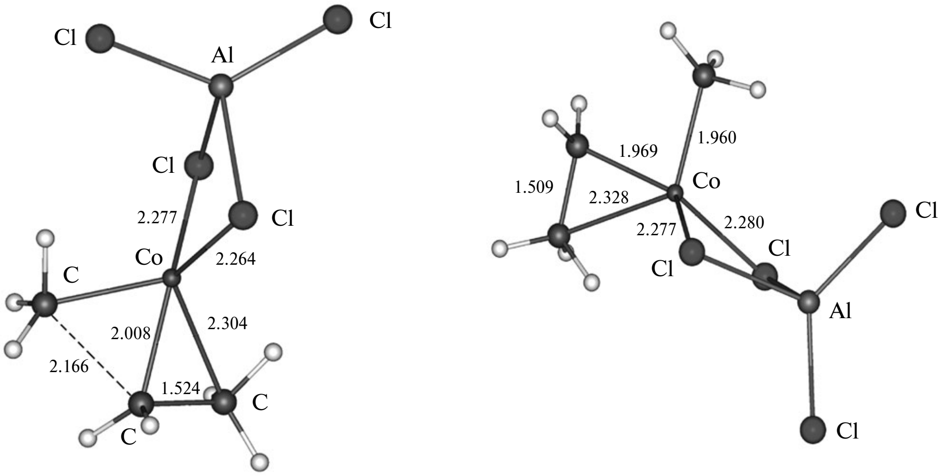
Fig. 3. Structures of the transition state **TS2** and the product of the C—C bond activation in propane molecule on the Co^+ cation (ΔE and ΔG, kcal mol^{-1} are the energies given relative to the corresponding characteristics of the model complex $Co^+C_3H_8$). Obtained from PBE/TZ2p calculations.

fragment followed by elimination of alkane molecule. For isolated atomic ions, such processes are usually treated as intramolecular transfer of a hydrogen atom from one alkyl fragment to another.[12,26—28]

In this case, transformations of hydrocarbons that occur in the coordination sphere of the complex cation $CoAlCl_4^+$ are precluded by steric hindrance. However, our calculations showed that transfer of hydrogen atom to intermediate **IM1** can occur in the interaction of **IM1** with the alkylmetal complex formed in the activation of alkane C—H bond.

Alkane C—H bond activation and formation of bimetallic alkyl complexes. As mentioned above, activation of alkane C—H bonds under the action of aluminum halides and cobalt halides may follow the alkyl pathway and result in alkylmetal derivatives (see Eq. (2)). We calculated reactions of propane with the experimentally detected ionic bimetallic complexes of aluminum chloride with cobalt chloride (**1a**,**b**) taking into account the fact that they begin with the formation of cationic complexes of propane $C_3H_8 \cdot CoAlCl_4^+$ (see above).

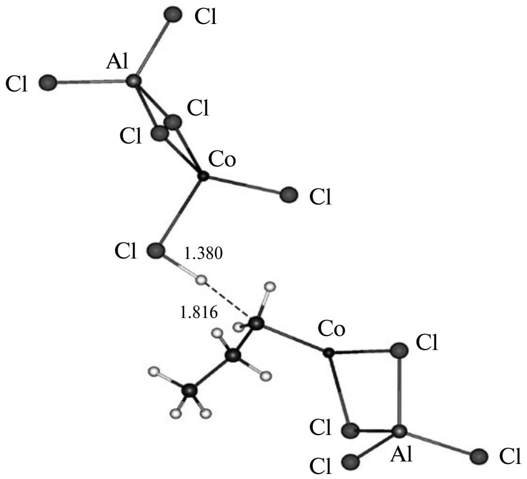
It was found that the reaction of the associate $C_3H_8 \cdot CoAlCl_4^+$ with the anion $CoAlCl_6^-$ proceeds *via* pre-reaction complex **3**. According to calculations, the thermodynamic effect of the formation of complex **3** almost compensates the endothermicity of the formation of ionic associates $CoAlCl_6^-$ and $CoAlCl_4^+$ from two molecules of the neutral bimetallic complex $CoCl_2 \cdot AlCl_3$:



TS3
$\Delta E = 25.5$; $\Delta G = 25.0$

IM1
$\Delta E = 24.1$; $\Delta G = 22.2$

Fig. 4. Structures of the transition state **TS3** and product **IM1** of activation of C—C bond in propane molecule on cluster $C_3H_8CoAlCl_4^+$ (ΔE and ΔG, kcal mol^{-1}, are the energies determined relative to complex **2d**). Calculated by the PBE/TZ2p method.



TS4
$\Delta E = 23.7$; $\Delta G = 21.6$

Fig. 5. Structure of transition state **TS4** between complexes **3** and **3a** on cluster $C_3H_8CoAlCl_4^+$ (ΔE and ΔG, kcal mol^{-1}, are the energies given relative to the corresponding characteristics of complex **3**). Calculated by the PBE/TZ2p method.

$$2\,CoCl_2 \cdot AlCl_3 + C_3H_8 \longrightarrow \underset{\mathbf{3}}{[C_3H_8 \cdot CoAlCl_4^+ + CoAlCl_6^-]} \qquad (3)$$

$(\Delta E = -0.2 \text{ kcal mol}^{-1})$

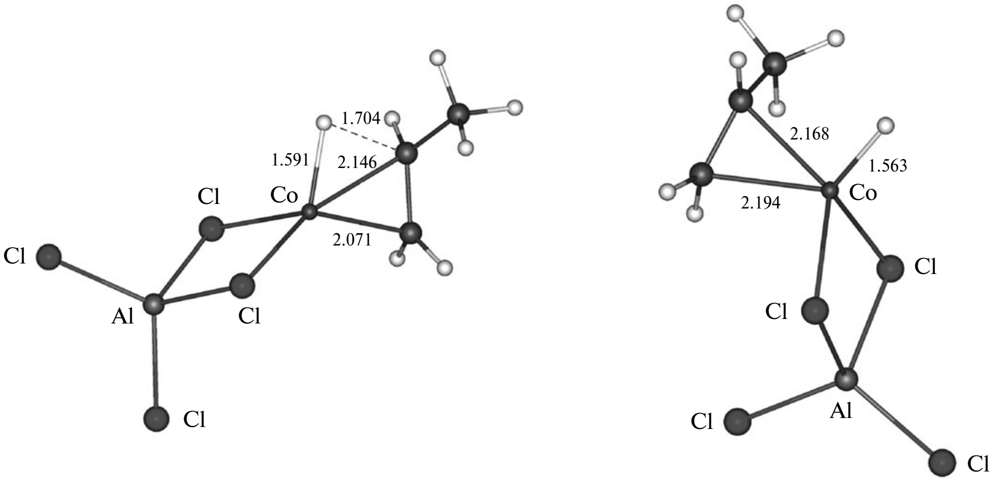
Further interaction within complex **3** may result in transfer of a proton from the propane molecule to the chlorine atom of the anionic fragment $CoAlCl_6^-$. The reaction proceeds *via* transition state **TS4** (see Fig. 5) with an energy barrier ΔG of 21.6 kcal mol^{-1} and involves the formation of an intermediate (complex **3a**) which then decomposes to two bimetallic complexes $HCoAlCl_6$ (**4**) and $C_3H_7CoAlCl_4$ (**5**).

Calculations for the alkylmetal complex $C_3H_7CoAlCl_4$ (**5**) also revealed the possibility of β-elimination of hydrogen atom *via* the transition state **TS5** (Fig. 6) with an activation barrier ΔG of 17.7 kcal mol^{-1} resulting in complex **5a** with a relative energy of 7.7 kcal mol^{-1}. The hydride hydrogen atom bears a small negative charge $q = -0.115$ a.u. The interaction of the labile complex **5a** with the propane molecule activated at a C—C bond in the cationic complex $C_3H_8 \cdot CoAlCl_4^+$ (**IM1**) may lead to unusual products of alkane transformations.

Formation of ethane molecule. Consider the formation of alkane metathesis products in the reaction of intermediate **IM1** with the bimetallic alkyl complex $C_3H_7CoAlCl_4$ (**5**). The calculated energy diagram of the overall reaction is shown in Fig. 7. Pathway *I* corresponds to transformations within the cationic complex $C_3H_8 \cdot CoAlCl_4^+$ resulting in **IM1**. Pathway *II* illustrates the formation of complex **5a** from structure **5**. Then, both routes merge.

From Fig. 7 it follows that the highest activation energies are required for the reactions of oxidative addition of propane at the C—C bond and β-elimination of hydrogen in the alkylmetal complex with the formation of complex **5a** (see above). Subsequent reactions leading to elimination of ethane molecule occur almost barrierlessly (relative to the starting complexes).

The reaction of intermediate **IM1** with complex **5a** begins with the formation of the pre-reaction complex **6** whose structure is shown in Fig. 8. The stabilization energy of this complex is 10.8 kcal mol^{-1}. Then, the reaction proceeds *via* transition state **TS6** (see Fig. 8) with an acti-



TS5
$\Delta E = 19.1$; $\Delta G = 17.7$

5a
$\Delta E = 8.8$; $\Delta G = 7.7$

Fig. 6. Structures of transition state **TS5** and product **5a** of the β-elimination reaction of hydrogen atom in the propyl radical of the complex $C_3H_7CoAlCl_4$ (**5**) (ΔE and ΔG, kcal mol^{-1}, are the energies given relative to the corresponding characteristics of complex **5**). Calculated by the PBE/TZ2p method.

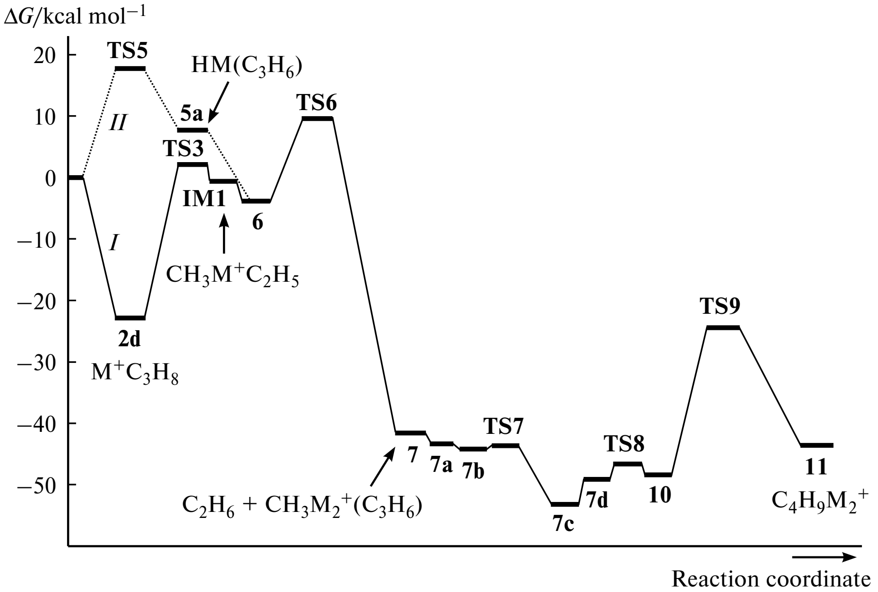
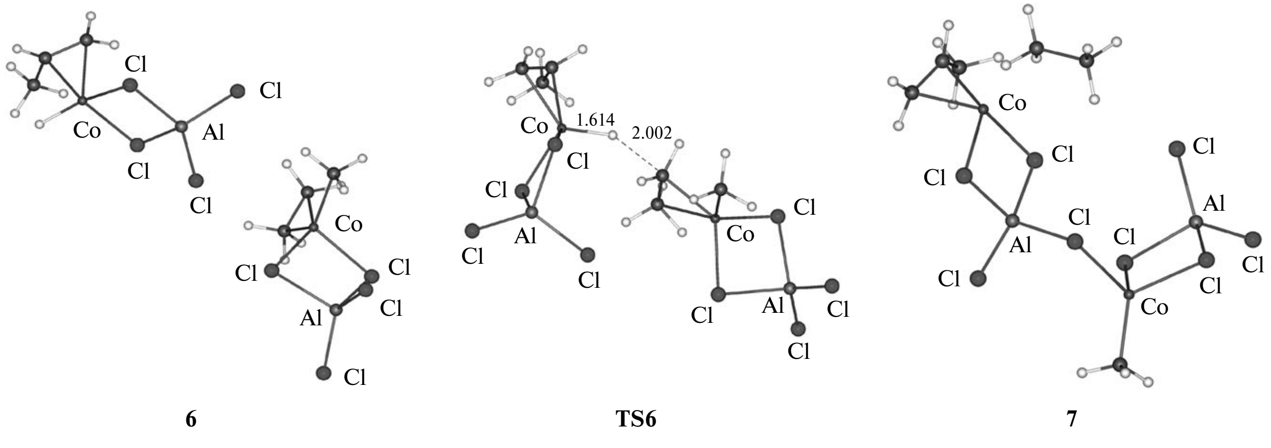


Fig. 7. Energy diagram illustrating the stages of propane transformation on the bimetallic ionic cluster $CoAlCl_4^+$. The energies are given relative to the corresponding characteristics of the propane molecule and ionic complex $[CoAlCl_4^+]$ (for route *I*) or bimetallic alkyl complex $C_3H_7CoAlCl_4$ (**5**) (for route *II*). As complex **6** is formed, both routes merge. Obtained from PBE/TZ2p calculations. M = $CoAlCl_4$.

vation barrier of 13.4 kcal mol^{-1} and is completed by the formation of product **7** (its energy decreases to $\Delta G = -37.7$ kcal mol^{-1} relative to structure **6**) and elimination of ethane molecule.

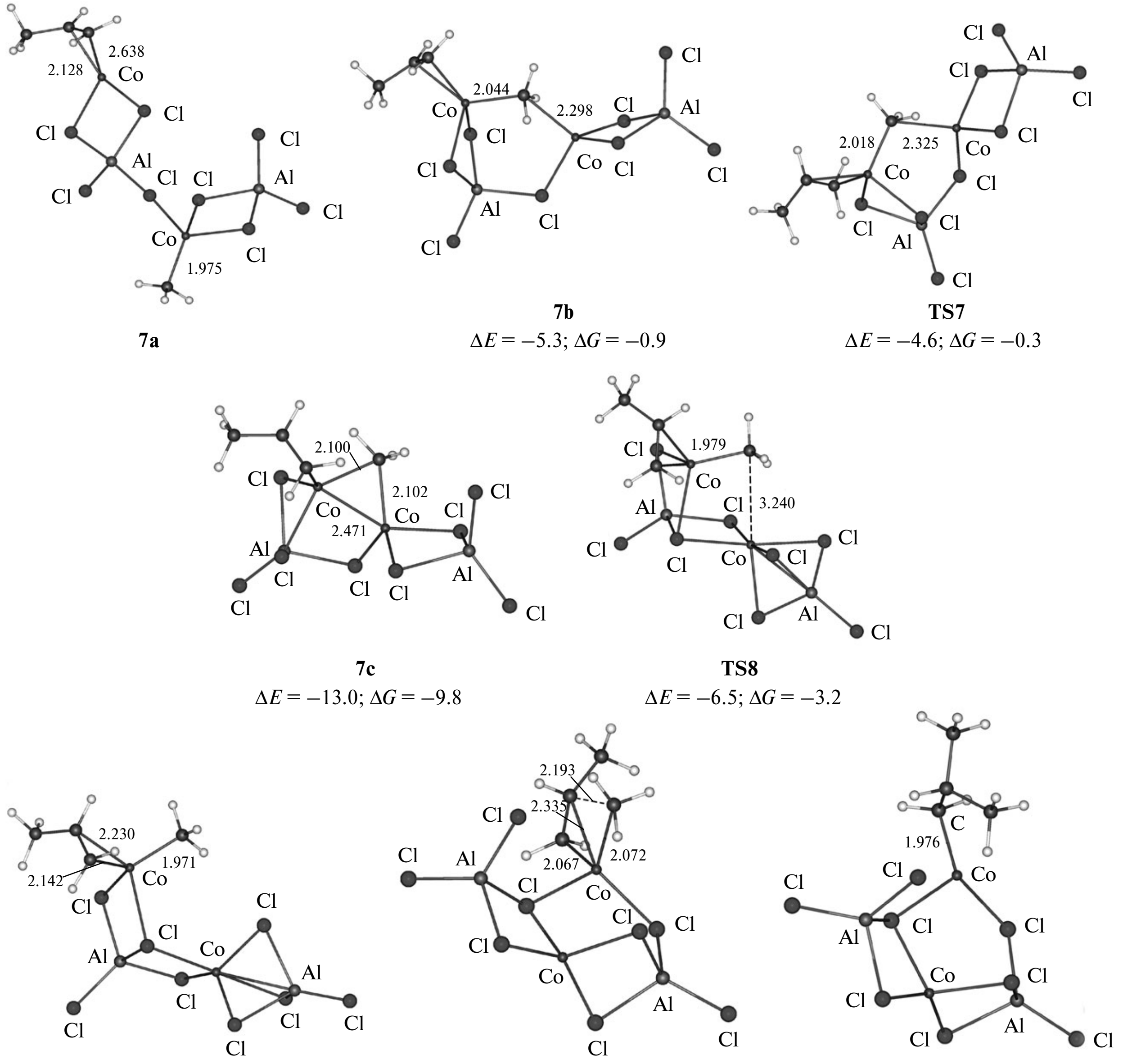
Formation of a C_4 product. Further pathway of reactions of complex **7** is of particular interest because it leads to a butyl radical, the second product of propane transformations. A number of intermediates were located on this pathway. For the sake of simplicity, the ethane molecule eliminated upon the formation of structure **7** was left out of consideration and we studied only the reactions involving complex **7a**. The structures formed in the course of its transformations are shown in Fig. 9 and the corresponding energy diagram is presented in Fig. 7.

From Figs 7 and 9 it follows that cluster **7a** undergoes an intramolecular rearrangement with the formation of structures **7b**,**c** containing bridging bonds between the methyl group and two Co atoms. It should be noted that the rearrangement **7b**→**7c** proceeds *via* transition state **TS7** with a very low energy barrier. The next reaction from structure **7d** with a close energy passes *via* transition state **TS8** and results in complex **10** (see Figs 7 and 9). Subsequent addition of the Me group within the coordination sphere of one cobalt atom to the olefin fragments (π-complex) leads to the bimetallic cluster containing the iso-



6 **TS6** **7**

Fig. 8. Structures of the pre-reaction complex **6**, transition state **TS6**, and product **7** of the reaction of hydrogen transfer between complexes **5a** and **IM1** resulting in the formation of ethane molecule. Obtained from PBE/TZ2p calculations.



7a

7b
$\Delta E = -5.3$; $\Delta G = -0.9$

TS7
$\Delta E = -4.6$; $\Delta G = -0.3$

7c
$\Delta E = -13.0$; $\Delta G = -9.8$

TS8
$\Delta E = -6.5$; $\Delta G = -3.2$

10
$\Delta E = -7.4$; $\Delta G = -5.0$

TS9
$\Delta E = 16.0$; $\Delta G = 19.0$

11
$\Delta E = -4.7$; $\Delta G = -0.2$

Fig. 9. Structures of transition states **TS7**—**TS9** and intermediates on the parthway of transformations of complex **7a** resulting in the bimetal-butyl ionic complex **11** (ΔE and ΔG, kcal mol^{-1}, are the energies given relative to the corresponding characteristics of complex **7a**).

butyl radical (**11**) whose carbon chain is one carbon atom longer than that of propane. The reaction proceeeds *via* a transition state with an activation energy ΔG of 24.0 kcal mol^{-1}. This is the pattern of formation of the second product of propane transformations on the bimetallic cluster of aluminum chloride with cobalt chloride.

Continuation of the catalytic cycle of alkane transformations. The pathways of subsequent transformations of the bimetallic alkyl cationic complex **11** of the general formula $(i\text{-}C_4H_9)M_2^+$ (M = $CoAlCl_4$) can be represented as follows. On the one hand, the isobutylmetal cation just formed can abstract a proton from the adjacent complex $HCoAlCl_6$ (**4**) and thus allow the isobutane molecule to eliminate. On the other hand, the reaction with the adjacent bimetallic anion $CoAlCl_6^-$ should lead to overall charge neutralization. The second process seems to be more probable because of a greater energy gain.

After charge neutralization, the isobutylmetal complex **11** is analogous to complex **5** with a longer metal-chlorine fragment $(i\text{-}C_4H_9M_3Cl_2)$. Because of this, the reactions considered above for complex **5** can also be characteristic of complex **11**. In complex **11**, β-elimination of H atom analogous to the reaction **5** → **5a** (see Fig. 6) should proceed easier than in the propyl-containing complex **5**.

Subsequent reactions of the isobutylmetal cluster $(i\text{-}C_4H_8)HM_3Cl_2$ (structural analog of **5a**) with the complex $C_3H_8 \cdot CoAlCl_4^+$ (and intermediate **IM1** derived from it) will lead to elimination of a new ethane molecule. In turn, transformations similar to the reactions **7** → **11** (see Fig. 9) will result in isopentyl radical in the coordination sphere of the cobalt atom. The process can schematically be described as follows:

$$M^+C_3H_8 + i\text{-}C_4H_9M_3Cl_2 \longrightarrow$$

$$\longrightarrow C_2H_6 + (i\text{-}C_5H_{11})[M_4Cl_2]^+, \qquad (4)$$

$M = CoAlCl_4$.

The sequence of reactions will continue until the reaction of the bimetallic alkyl complex with $HCoAlCl_6$ occur with elimination of a long branched hydrocarbon.

Thus, our calculations of active complexes and pathways of propane transformations under the action of the aluminum chloride—cobalt chloride clusters showed that

1) alkane C—C and C—H bonds are activatied in the reactions with ionic bimetallic complexes of aluminum chloride with cobalt chloride, which are formed in structurally organized clusters comprising molecular complexes of metal halides;

2) activation of alkane C—H bonds follows the alkyl pathway involving the formation of bimetallic alkyl complexes;

3) cationic bimetallic complexes of aluminum chloride with cobalt chloride may cause cleavage of alkane C—C bonds followed by oxidative addition of the alkane to the bimetallic complex;

4) reactions of activated hydrocarbon fragments bound to transition metal atoms in the cobalt chloride—aluminum chloride clusters may result in alkane metathesis products.

The calculated pathways of alkane reactions with bimetallic complexes of aluminum chloride with cobalt chloride provide a better insight into the regularities of low-temperature conversion of alkanes. This first of all concerns the experimentally established fact[16—17] that the prerequisite for the low-temperature activation of alkanes is pre-formation of clusters of definite composition from molecular complexes of aluminum halide with cobalt halide. Our theoretical study confirmed that at least two clusters of bimetallic complexes are involved in the formation of products of alkane transformations.

In addition, calculations revealed possible routes of formation of such products of *n*-alkane transformations that are not typical of catalysis by Lewis acids, namely, formation of non-stoichiometric amounts of *n*-alkanes whose carbon chains are one carbon atom shorter than those of the starting alkanes under the action of aluminum chloride—cobalt chloride complexes.[14] For instance, low-temperature (170—230 K) conversion of *n*-octane affords *n*-heptane (up to 30—40%) and monomethylheptanes (isomerization products of *n*-octane) as the major products; the content of light hydrocarbons is at most 5%.

Calculations showed that propane reactions with the experimentally detected bimetallic ionic complexes with energy barriers of at most 25 kcal mol^{-1} may result in ethane whose chain is one carbon atom shorter and simultaneous elongation of the carbon chain of the bimetallic alkyl complex. Successive involvement of additional propane molecules in the reaction with the growing bimetallic alkyl complex leads to elimination of new ethane molecules.

Possible routes of alkane conversion under the action of aluminum chloride—cobalt chloride complexes resulting in skeletal isomerization products will be considered elsewhere.

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