Russian Journal of Organic Chemistry, Vol. 37, No. 12, 2001, pp. 1675–1682. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 12, 2001, pp. 1755–1762.
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MNDO/PM3 Study of the Reaction Mechanism between Methane and Complexes Generated in $Br_2{\cdot}AlBr_3$ System*

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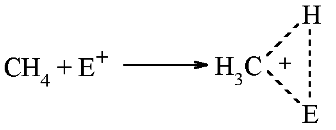
Received February 10, 2000

Abstract—Potential energy surface (PES) of systems $AlBr_5$ and $AlBr_5$ + CH_4^+ were investigated by MNDO/PM3 method. All the five donor-acceptor complexes $Br_2{\cdot}AlBr_3$ with no barrier add to methane providing multiple adducts with various localization of interactions and with different conformations. However further transformations occur only with adducts of two complexes $Br_2{\cdot}AlBr_3$ possessing considerable ionic character. On the reaction path resulting in CH_3Br and HBr as intermediates function bromonium type complexes $CH_3BrH^+{\cdot}AlBr_4^-$ and the intermediates on the path leading to CH_2Br_2 and H_2 are the complexes with 3c–2e bond of H_2 quasi-molecule with the C atom of bromomethyl cation $H_2C(H{-}H)Br^+{\cdot}AlBr_4^-$. Potential barriers on both reaction paths are about 30 kcal mol^{-1}, and the transition states (TS) are analogous to the classical 3c–2e TS (Olah scheme) with an electrophile attack on a CH bond and to the recently suggested TS with an electrophile attack on an unshared electron pair of the carbon atom in the nonclassical methane $H_2C(H{-}H)$ respectively.

Since the beginning of nineteen seventies the electrophilic activation of alkanes has been extensively investigated. Especially valuable contribution thereto provided D. Olah [1, 2].

The classical mechanism of alkane reactions with electrophiles is reliably proved [1, 2] for protolytic transformations or the cases with a cation as electrophile; it involves an attack of the electrophile E^+ on a σ-bond C–H or C–C to yield a three-center two-electron (3*c*–2*e*) intermediate or transition state (Scheme 1).

Scheme 1.



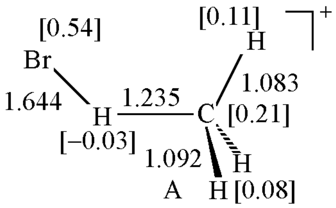
Another mechanism of alkane activation was suggested in [3, 4]. Basing on the *ab initio* quantum-chemical calculations for reactions of a nitrosonium cation with methane [3] and ethane [4] it was concluded that alkane nitrosation mechanism was described by Scheme 2 involving attack of NO^+ cation directly on a carbon atom with a synchronous formation of a 3*c*–2*e* bond of this atom with a quasi-molecule H_2.

Scheme 2.

$$CH_4 + NO^+ \rightarrow [H_2C(HH)NO]^+$$

Olah *et al.* [5] questioned the validity of Scheme 2 since the NO^+ cation was a weak electrophile and actually methane nitrosation with NO^+ did not occur in the absence of additional electrophiles.

In extension of quantum-chemical investigation on the nature of new generation of superelectrophiles [6, 7] we regarded active systems mBr$_2{\cdot}n$AlBr$_3$ [8] and $Br_2{\cdot}AlBr_3$ [9] and found generated therein complexes containing positively-charged bromine.



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Bond lengths are given in Å, the charge values on the atoms are given in parentheses in a.u. Calculation by MNDO/PM3 procedure.

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[*] The study was carried out under financial support from the Russian Foundation for Basic Research (grant no. 98-03-32274).

We started the study of alkane activation mechanism with these complexes by an example of Br^+ + CH_4 model system [10]. Quite unexpectedly it turned out that in this system the reactions were described with schemes including cation A arising with no barrier and containing a hypervalent hydrogen.

As far as we know this is the first example of formation of an intermediate $R–H–E^+$ with acyclic 3*c*–2*e* bond at the electrophilic alkane activation (in the organometallic chemistry of alkanes the complexes RH···M are well known since the later nineteen seventies).

A singular result of this study consisted in establishing that the reaction in the system Br^+ + CH_4 affording hydrogen bromide and methyl cation might occur along Scheme 3 excluding the stage of formations of intermediates or transition states inherent to Olah scheme (Scheme 1). In other words, the classical Olah scheme of alkane electrophilic activation [1, 2] is not obligatory for such powerful superelectrophile as a “naked” Br^+ cation.

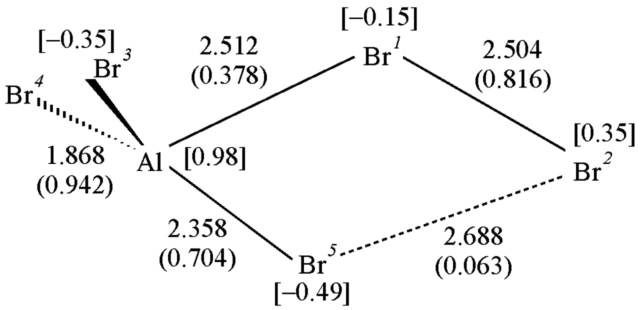
Scheme 3.

$$CH_4 + Br^+ \rightarrow [CH_3–H–Br]^+ \rightarrow CH_3^+ + HBr$$

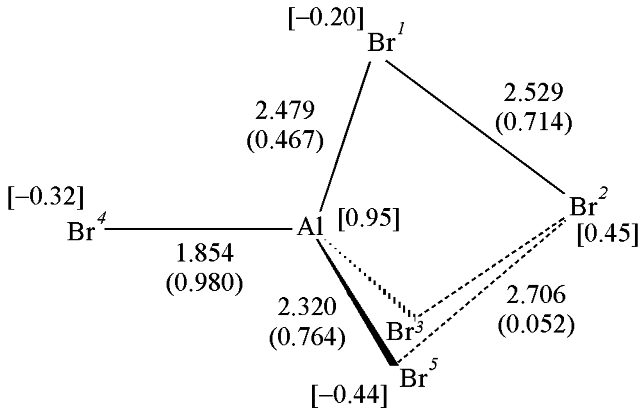
In extension of investigation on the nature of alkane activation with new superelectrophilic systems and in order to test whether the above mechanism is valid also for weaker electrophiles where a bromine atom with sufficiently large positive charge is contained in a neutral system we have studied the reactions with methane of complexes generated in a system $Br_2·AlBr_3$ that is active in reactions with alkanes [11].

Calculation procedure. The calculations were performed by MNDO/PM3 [12] procedure with full optimization of geometrical parameters by software MOPAC 5.10 and GAMESS [13] on a work station DEC 3000 AXP-400X. The local minima were determined by UHF approximation (to all the minima corresponded systems with closed electron orbitals). The geometry of transition states was optimized by Schlegel method [14]. The character of stationary points was refined by calculation of eigenvectors of Hessian matrix.

Discussion of results. In the preceding communication [9] we presented the simulation results of potential energy surface (PES) for the systems $[AlBr_5]$ (**I**) and $[AlBr_5 + CH_4]$ (**II**). In system **I** were revealed 5 isomers of donor-acceptor complexes $Br_2·AlBr_3$ corresponding to local minima on PES. All the isomers add to methane molecule with no barrier to afford a multitude of adducts that are distinguished both by interaction localization and conformation. The investigation of potential curves along various reaction coordinates for many among these complexes showed that the majority of the complexes did not take part in further transformations. Actually, the increase of the distance between components involved in these adducts along various reaction coordinates led only to the original systems, and the forced approach resulted in sharply growing potential energy with no transition to new local minima. For further study were promising only the adducts of methane with complexes **Ia, b** of system **I** (Fig. 1) that possessed a pronounced ionic character. These are complexes **IIa, b** and **IIIa, b** (Fig. 2).

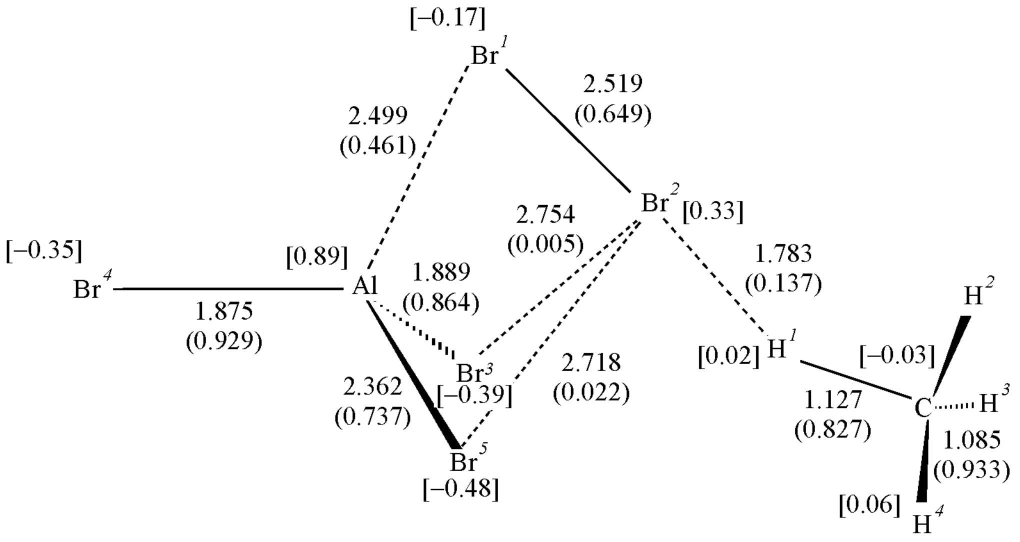


Ia (C_s)
ΔH_f −100.9 kcal mol^{-1}
$AlBr^2$ 4.177; $AlBr^1Br^2$ 112.8,
Br^1AlBr^5 70.3 deg



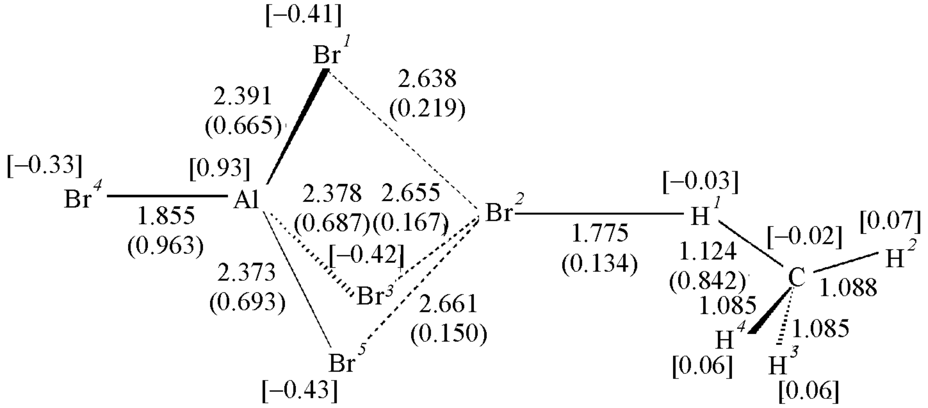
Ib (C_s)
ΔH_f −94.6 kcal mol^{-1}
$AlBr^2$ 3.821 (0.027); $AlBr^1Br^2$ 99.5,
Br^1AlBr^4 135.4 deg

Fig. 1. Structures of complexes corresponding to local minima in $AlBr_5$ system; bond lengths (Å), bond orders (a.u., in parentheses), effective charges on atoms (a.u., in brackets). The calculated bond length in the molecule Br_2 is 2.444 Å.



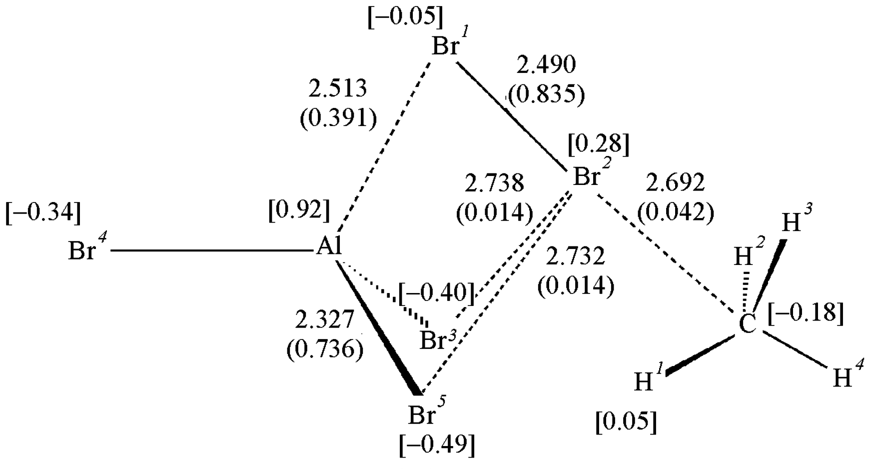
IIa (C_1)

ΔH_f –124.3 kcal mol^{-1}; AlBr^2 2.615 (0.071); AlBr^{1}Br^2 62.8, Br^{1}AlBr^4 110.3, CH^{1}Br^2 127.0 deg



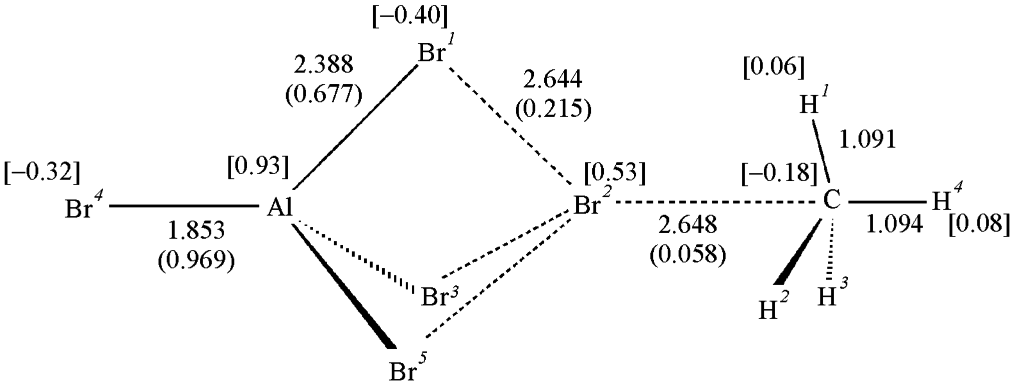
IIb (C_1)

ΔH_f –116.8 kcal mol^{-1}; AlBr^2 3.874 (0.024); CH^{1}Br^2 125.2 deg

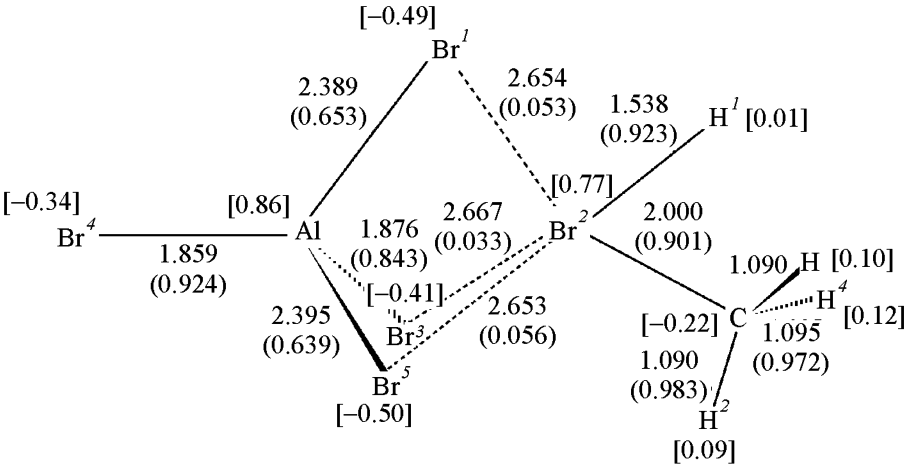


IIIa (C_1)

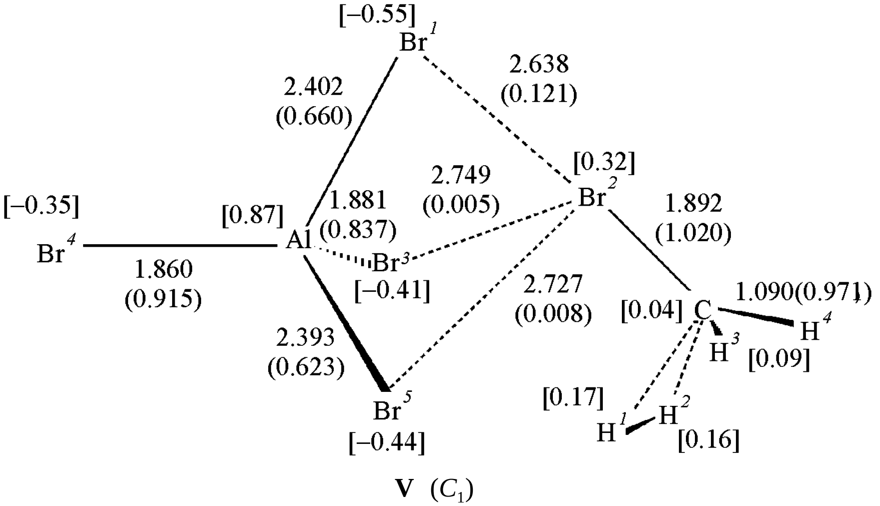
ΔH_f –122.7 kcal mol^{-1}; AlBr^2 2.616 (0.084); AlBr^{1}Br^2 63.06 deg



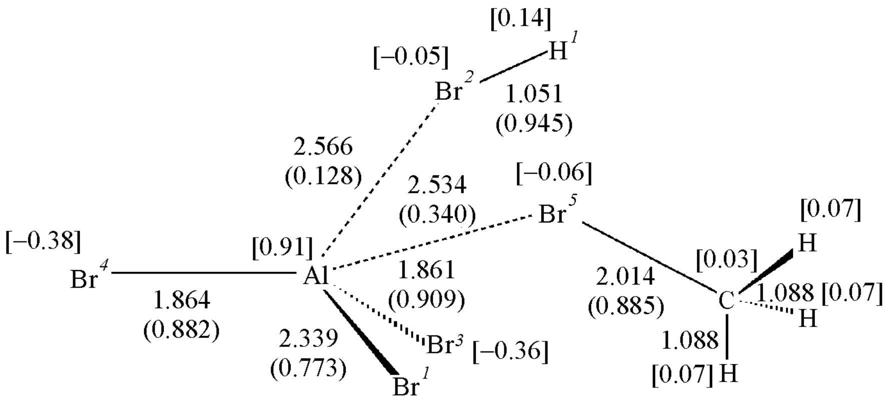
IIIb (C_{3v})
ΔH_f −114.9 kcal mol^{-1}
AlBr^2 3.843 (0.028)



IV (C_1)
ΔH_f −109.9 kcal mol^{-1}
AlBr^2 2.667 (0.033); $\mathrm{CBr}^2\mathrm{H}^1$ 94.3 deg



V (C_1)
ΔH_f −101.5 kcal mol^{-1}
$\mathrm{H}^1\mathrm{H}^2$ 0.768 (0.669), C···H^1 1.575 (0.261), CH^2 1.566 (0.267), AlBr^2 2.622 (0.054)



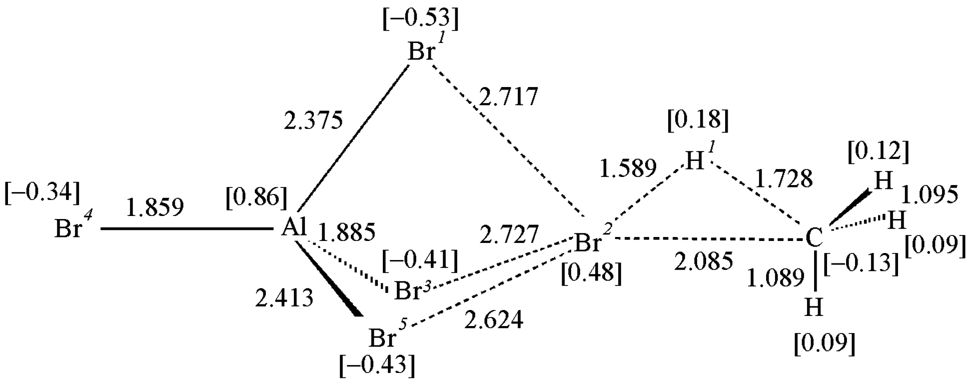
VI (C_1)
ΔH_f −120.9 kcal mol^{-1}

Fig. 2. Structures of complexes corresponding to local minima in the [$AlBr_5$ + CH_4] system; notations as in Fig. 1.

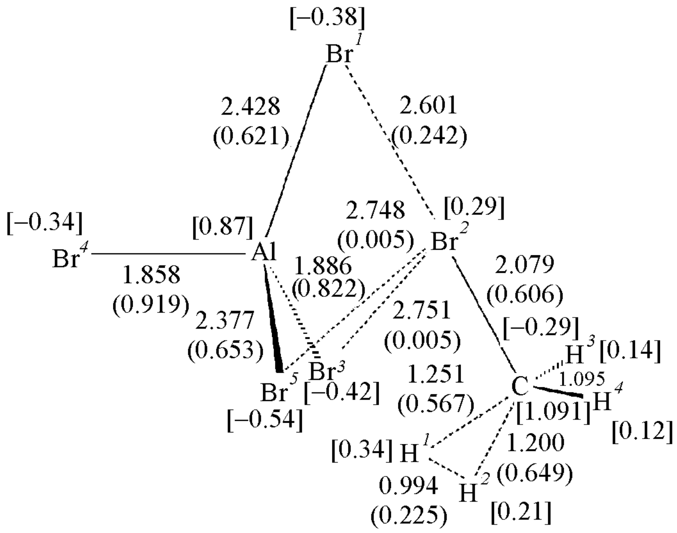
Complexes **IIa, b** arise from no-barrier addition of electrophiles **Ia, b** to the atom H of methane, and complexes **IIIa, b** form at no-barrier attack on methane by complexes **Ia, b** along the C–H bond from the C atom side. Complexes **IIa, b** arise quite similarly to formation of cation A with acyclic 3*c*–2*e* bond C–H–Br$^+$ in the model system Br$^+$ + CH_4. However the principal difference should be noted between potential curves along reaction coordinate R_c = C···Br^2 for cation A, on the one hand, and complexes **IIa, b**, on the other hand. In cation A the bromine atom moving away from carbon atom entrains also a hydrogen atom, and the hydrogen bromide and the methyl cation form bypassing the transition states characteristic of Olah scheme as we have already mentioned. Yet in complexes **IIa, b** the movement of the Br atom away from the C atom leads to the initial systems. However we succeeded to find for complexes **IIa, b** and **IIIa, b** relation to the other types of complexes also arising in system **II**. The cases in point are complexes of bromonium type that correspond to electrophiles insertion into the C–H bond of methane, and also complexes formally corresponding to products of electrophilic attack on C atom in methane, complexes possessing 3*c*–2*e* bond between this atom and a quasi-molecule H_2.

Complexes **IIa, b** and **IIIa, b** that form with no barrier at electrophile **Ia, b** approach to methane in the course of the further decrease in the Br^2···C distance transform into bromonium-type complexes (one among these, complex **IV**, is given in Fig. 2). These complexes easily undergo interconversion (potential barriers amount to ~5 kcal mol^{-1}). However it should be noted that potential curves along the reaction coordinate R_c = Br^2···C suffer jumps in the distance region R_c less than that in the complexes **IIa, b** and **IIIa, b**. The smooth potential curves for transition from the initial complexes **II, III** to bromonium ones were obtained along reaction coordinate R_c = C···H^1 (moving of atom H^1 away from C atom) and R_c = ∠Br–C–H^1 (increase in this angle resulted in decreasing distance Br^2···C and increasing distance C···H^1). The maximum points on these curves were refined in SADPOINT mode. All the transition states obtained were of the same type and close in energy. These are typical 3*c*–2*e* transition states of Olah Scheme (1). On Fig. 3 is shown the lowest in energy among these transition states **VII** that corresponds to interconversions **IIa** **IV**.

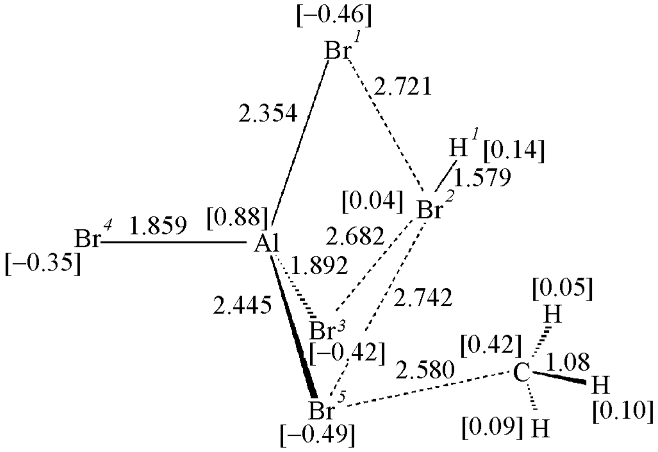
We failed to find the reaction coordinate for conversion of initial complexes **IIa, b** and **IIIa, b** or bromonium complexes into complexes with a quasi-molecule H_2 (similar to the complex described in Scheme 2). The calculation of the latter was carried out with the original approximation to the geometry, on the one hand, of the known structure of the hydrogen molecule complex with the carbon atom of the bromomethyl cation $BrCH_2(H{-}H)$⌉$^+$ [10], and on the other hand, of the structures of complexes **Ia, b** in such manner that the terminal Br^2 atom should be common. We succeeded in transition from the obtained complexes with a quasi-molecule H_2 (one of them, complex **V**, is shown on Fig. 2) to complexes **IIa, b** by increasing the distance Br^2···C. The structure of the transition states for the maximum points on the potential curves was refined in SADPOINT mode. (On Fig. 3 is shown the structure of transition state **VIII** corresponding to interconversion **IIa** ⟷ **V**).



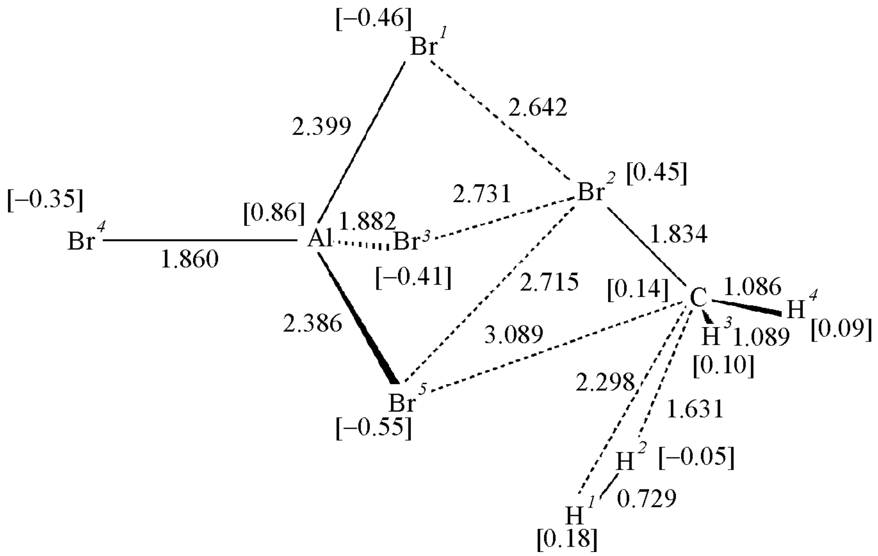
VII (C_1) TS (**IIa** ↔ **IV**); ΔH_f −98.6 kcal mol^{-1}; AlBr^2 2.646



VIII (C_1) *TS* (**IIa** ↔ **V**)
ΔH_f −95.9 kcal mol^{-1}; Al Br^2 2.615 (0.067)



IX (C_1) *TS* (**IV** ↔ **VI**)
ΔH_f −91.5 kcal mol^{-1}; AlBr^2 2.609, CBr^2 2.551



X (C_1) TS (**V** ↔ H_2 + H_2CBr_2·$AlBr_3$)
ΔH_f −97.3 kcal mol^{-1}; AlBr^2 2.635

Fig. 3. Structures of transition states in the system [$AlBr_5$ + CH_4]; notations as in Fig. 1.

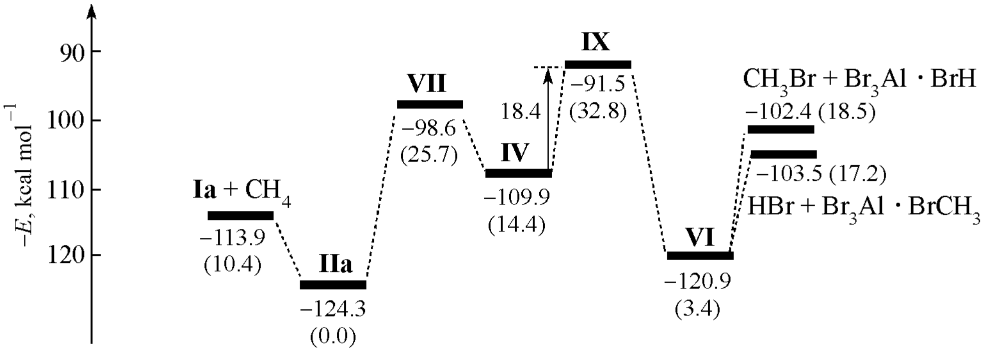


Fig. 4. Energy diagram of methane bromination.

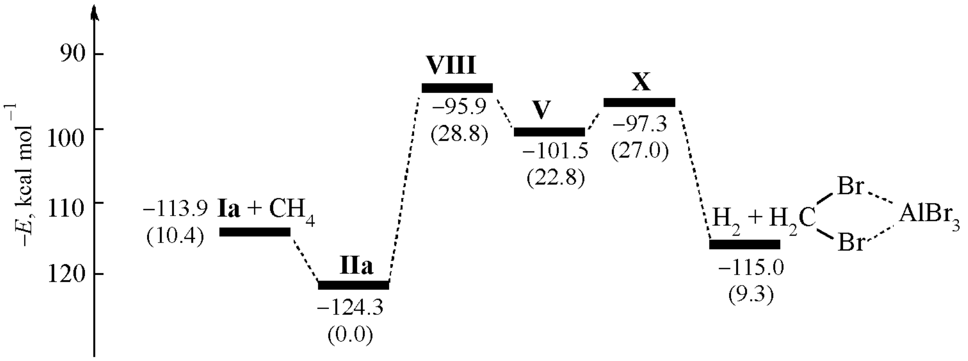


Fig. 5. Energy diagram of H_2 molecule elimination from a methane molecule.

Further transformations in the system [$AlBr_5$ + CH_4] (**II**) occur with bromonium complexes and with complexes containing quasi-molecule of hydrogen.

The increasing distance $Br^2\cdots C$ in the bromonium complexes results in HBr elimination from the methyl fragment, in coordination of the latter to one of bromine atoms in the anion $AlBr_4^-$ and finally in formation of $AlBr_3$ complexes with HBr and CH_3Br molecules (one of these complexes of five-coordinate aluminum, complex **VI**, is shown on Fig. 2). The formation enthalpy for the main conformers of these complexes is approximately equal to that of the initial complexes **IIa** and **IIIa** (–124.3, 122.7 kcal mol^{-1}), but potential barriers to the transformations with participation of bromonium complexes are fairly high. Estimation of energy on the paths of endothermic methane bromination

$$Br_2 + CH_4 \rightarrow HBr + CH_3Br\ -12.3\ \text{kcal mol}^{-1}$$

is complicated by the great number of conformers both of the initial and final complexes occurring on the paths of this reaction. We restricted the description by giving on Fig. 4 the transformation path where we found the lowest potential barriers (the structure of transition state **IX** of conversion **IV** → **VI** is shown on Fig. 3).

Even less energy is required by reaction resulting in formation of hydrogen and dibromomethane molecules.

$$Br_2 + CH_4 \rightarrow H_2 + Br_2CH_2\ -3.5\ \text{kcal mol}^{-1}$$

The potential barriers for this reaction involving complexes with a quasi-molecule H_2 are also considerably high. One of the reaction paths is shown in Fig. 5 (transition state **X** for hydrogen elimination from complex **V** is depicted on Fig. 3).

Thus the study performed revealed among the numerous adducts of complexes $Br_2{\cdot}AlBr_3$ with methane formed with no barrier several complexes capable of further transformations. These are methane adducts with two complexes $Br_2{\cdot}AlBr_3$ (**Ia, b**) that possess a pronounced ionic character. Methane activated with these electrophiles was able to form bromonium complexes along the pathroute including 3*c*–2*e* transition states characteristic of the classical Olah scheme, and also was able to afford complexes with 3*c*–2*e* bond of H_2 with C atom of the bromomethyl cation solvated with $AlBr_4^-$ gegenion.

The methane bromination with HBr elimination unlike the situation in the model system $Br^+ + CH_4$ occurs only via bromonium intermediates, and elimination of a hydrogen molecule and dibromomethane formation proceeds with participation of complexes with a H_2 quasi-molecule (Fig. 5). Although both reactions do not require large energy consumption the potential barriers on their paths are fairly high (about 30 kcal mol^{-1}).

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