Mechanism of methane activation by electrophiles generated in the $AlBr_5$ system: an MNDO/PM3 study of the potential energy surface of the $[AlBr_5 + CH_4]$ system

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Fragments of the potential energy surfaces (PES) of the $AlBr_5$ (I) and $[AlBr_5 + CH_4]$ (II) systems were studied by the MNDO/PM3 method. Five local minima corresponding to $Br_2 \cdot AlBr_3$ donor-acceptor complexes were found on the PES of system I. Two of these complexes have a pronounced ionic character. In system II, among the products of barrierless addition of $Br_2 \cdot AlBr_3$ complexes to CH_4, the methane molecule is activated only in two complexes. These are products of the attack of the most electrophilic $AlBr_5$ complexes on a H atom of the methane molecule. The potential barriers to conversion of these products into complexes with structures formally corresponding to the products of the attack of electrophiles on a C—H bond (the Olah scheme) or the C atom of methane molecule (the Schreiner scheme) were calculated.

Key words: methane, bromine, aluminum bromide, complexes $Br_2 \cdot AlBr_3$, superelectrophiles; mechanism of electrophilic activation of alkanes; quantum-chemical calculations, MNDO/PM3 method, potential energy surface.

The classical mechanism of electrophilic activation of alkanes[1,2] includes the attack of electrophile (E^+) on the C—H or C—C σ-bonds with the formation of a three-center two-electron (3c-2e) intermediate or transition state according to the Olah scheme (for methane, see Scheme 1).

Scheme 1

Recently,[3,4] another mechanism was proposed for hypothetical reactions of methane or ethane with the nitrosonium cation NO^+. Based on the results of *ab initio* quantum-chemical calculations, the authors inferred that the attack of electrophile on the carbon atom rather than on the C—H bond with the synchronous formation of a 3c-2e bond between the C atom and the H_2 quasi-molecule (Scheme 2) is the key stage of nitrosation of methane[3] and ethane.[4]

Scheme 2

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

However, based on the fact that the NO^+ cation is a very weak electrophile and it does not enter into reactions with alkanes *per se*, Olah *et al.*[5] have cast doubt upon the realistic character of Scheme 2. In their opinion, the reaction of methane with the NOH^{2+} dication formed from the NO^+ cation in a protic acid should be considered. The *ab initio* quantum-chemical study[5] of the mechanism of this reaction reaffirmed that in this case, as well as at $E^+ = OH^+$ or F^+, electrophilic activation of alkanes is described by Scheme 1.

In the last decade, new types of superelectrophilic complexes highly active in reactions with alkanes have been found.[6–11] In a continuation of our studies on the nature of active organic and inorganic aprotic superacids[12–14] (in particular, those generated in $mBr_2 \cdot nAlBr_3$ systems, where m and n are integers[13]), we have considered the mechanism of their activating effect on alkanes taking a $[Br^+ + CH_4]$ model system as an example.[15] We have found that the attack of the Br^+ cation on the methane molecule is described by Scheme 3, which differs from both Scheme 1 (attack on the C—H bond) and Scheme 2 (attack on the C atom) and includes a barrierless coordination of the electrophile (Br^+) to a hydrogen atom of the methane molecule with the formation of complex **A** (the bond lengths are given in Å and the atomic charges obtained from MNDO/PM3 calculations are given in au in square brackets).

Scheme 3

$$CH_4 + Br^+ \longrightarrow [Me—H—Br]^+$$

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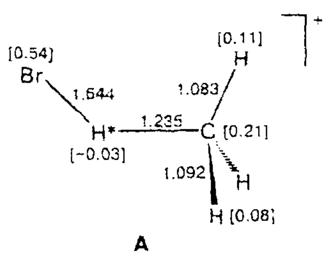


A

As far as we know, this is the first example of the formation of an R—H—E$^+$ intermediate with an acyclic 3c-2e bond in the course of electrophilic activation of alkanes (in organometallic chemistry of alkanes, the RH...M complexes have been known since the late 1970s).

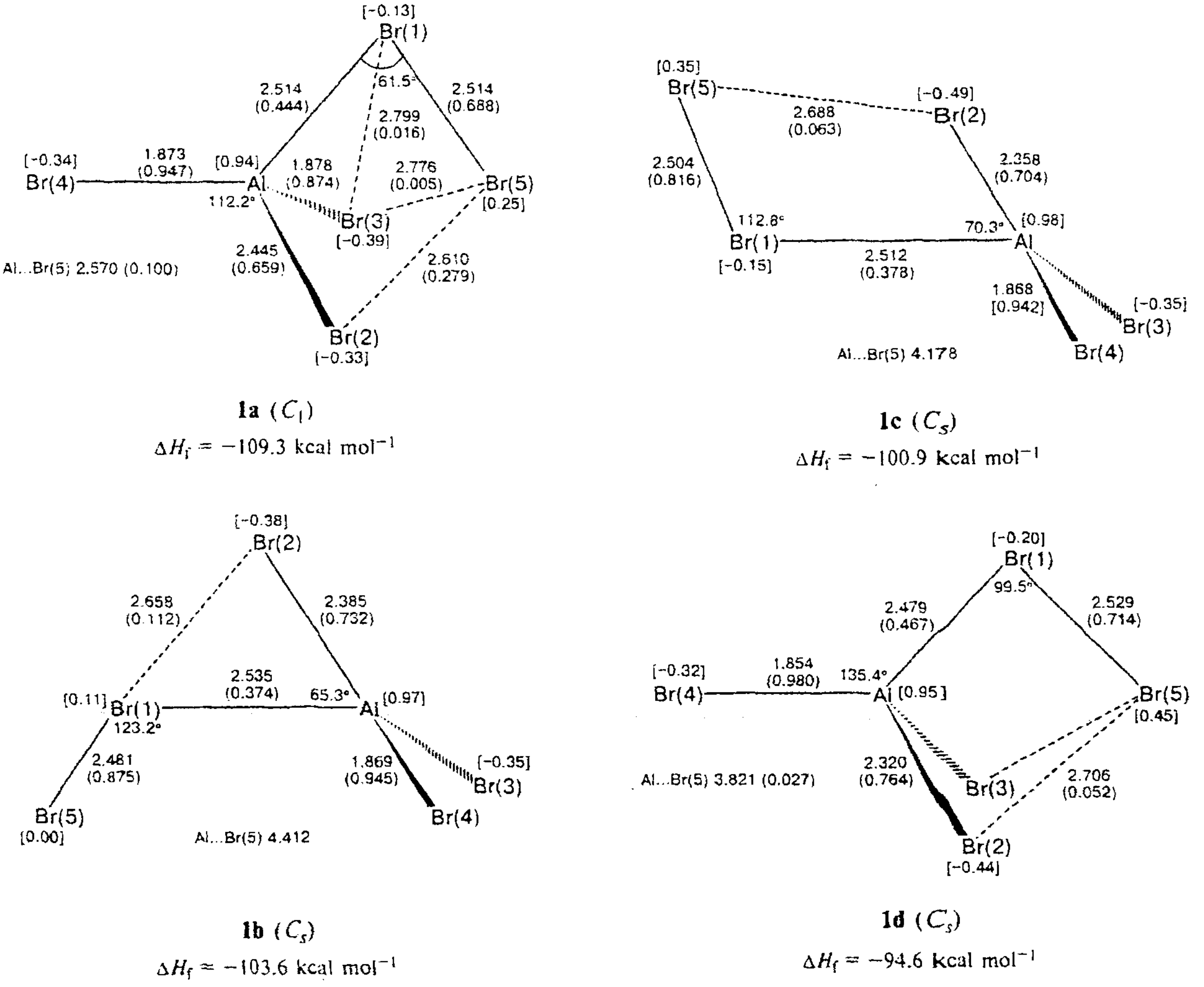
Nontrivial results obtained for such a strong electrophile as the "naked" Br$^+$ cation prompted us to study the reactions of methane with complexes generated in the $Br_2 \cdot AlBr_3$ system which is active in the reactions with alkanes.[10] As the first step of this investigation, in this work we analyze the potential energy surfaces (PES) of the $AlBr_5$ (I) and [$AlBr_5 + CH_4$] (II) systems in order to find local minima and to simulate the geometry and electronic structure of several transition states of transformations in system II.

Calculation procedure

Calculations were carried out by the MNDO/PM3 method[16] with full geometry optimization using the MOPAC 5.10 and GAMESS program packages[17] on a DEC 3000 AXP-400X workstation. Local minima (all of them correspond to systems with closed electron shells) were determined in the UHF approximation. The geometries of transition states were optimized by the Schlegel method.[18] The characters of stationary points were established by calculating the eigenvectors of the Hessian.

Results and Discussion

Complexes $Br_2 \cdot AlBr_3$. Detailed study of the PES of system I revealed five local minima corresponding to



1a (C_1)
$\Delta H_f = -109.3$ kcal mol^{-1}

1c (C_s)
$\Delta H_f = -100.9$ kcal mol^{-1}

1b (C_s)
$\Delta H_f = -103.6$ kcal mol^{-1}

1d (C_s)
$\Delta H_f = -94.6$ kcal mol^{-1}

Fig. 1. Structures of complexes corresponding to local minima in the $AlBr_5$ system. The bond lengths (in Å), bond angles (in degrees), bond orders (in au, figures in parentheses), and effective atomic charges (in au, figures in square brackets) are indicated.

donor-acceptor complexes $Br_2 \cdot AlBr_3$. Asymmetric complex **1a** (Fig. 1) corresponds to global minimum ($\Delta H_f = -109.3$ kcal mol^{-1}). Two local minima corresponding to complexes **1b** and **1c** with $\Delta H_f = -103.6$ and -100.9 kcal mol^{-1}, respectively (see Fig. 1), lie higher on the energy scale. The remaining two local minima have even much higher energies and correspond to donor-acceptor complexes, one of which is of low polarity and was described previously (see Ref. 13, complex **8a**), whereas the other is a highly polar complex **1d** ($\Delta H_f = -94.6$ kcal mol^{-1}, see Fig. 1). In these complexes, the Br(1)—Br(5) bond in the fragment corresponding to Br_2 molecule is slightly lengthened (according to MNDO/PM3 calculations, the equilibrium bond length in the Br_2 molecule is 2.444 Å).

Multiple interactions occur between the atoms of complex **1a**. In particular, this is the donor-acceptor bonding between the Br(1) atom of Br_2 molecule and the Al atom of the coordinatively unsaturated $AlBr_3$ molecule. In addition, the Br(5) terminal atom of the Br(1)—Br(5) fragment interacts with the Al atom, as well as electrostatic interactions occur of this bromine atom carrying a positive charge of 0.25 au with two out of three negatively charged Br atoms of the $AlBr_3$ fragment.

The next three local minima correspond to the complexes with mono- (**1b**), bi- (**1c**), and tridentate (**1d**) coordination of the Br(5) atom to the bromine atoms of the $AlBr_3$ fragment. These three complexes can be considered as donor-acceptor complexes between Br_2 and the coordinatively unsaturated $AlBr_3$ molecule which remains virtually planar in complexes **1b,c**. As a result of additional interactions, the donor-acceptor bond between the Br_2 fragment and $AlBr_3$ is tilted at an acute angle to the plane of the $AlBr_3$ fragment (the Br(1)—Al—Br(2) angles in complexes **1b** and **1c** are 65.3° and 70.3°, respectively). These complexes are two conformers. In complex **1b**, the Br(2) atom of the $AlBr_3$ molecule interacts with the Br(1) atom belonging to the Br_2 fragment and bonded to the Al atom. In complex **1c**, the Br(2) atom electrostatically interacts with the Br(5) terminal atom of the Br_2 fragment. The Br(5) terminal atom of the Br_2 fragment in complex **1d** forms two ionic bonds with bromine atoms of the $AlBr_3$ fragment which becomes nonplanar. In the $Br_2 \cdot AlBr_3$ donor-acceptor complexes, the $Br^{\delta+}...Br^{\delta-}$ ionic bonds and the Br(1)—Br(5) bond differ in the Wiberg indices (WI)[19] (the difference in WI is ~0.7 au) rather than in lengths (the difference in the bond lengths is ~0.2 Å). The formation of the $Br^{\delta+}...Br^{\delta-}$ ionic bonds with the Br(5) terminal atom of the Br_2 fragment is accompanied by a lengthening of the Br—Br bond, a decrease in its order, and, which is the most important, by an increase in the positive charge on the Br(5) terminal atom. Complexes **1c,d** in which the Br(5) atoms carry charges of +0.35 and +0.45 au, respectively, exhibit a pronounced ionic character.

Local minima in system $[AlBr_5 + CH_4]$. We will discuss only the structure of those intermediates in the $[AlBr_5 + CH_4]$* (II) system, which formally correspond to three directions of the attack of complexes **1a—d** on the methane molecule, namely, on an H atom, on the C atom, and on the C—H bond.

Complex **1a** corresponding to the global minimum on the PES of system I does not activate the methane molecule and forms only weak "solvates" $[CH_4 \cdot$ **1a**$]$. In these "solvates," the positively charged Br(5) atom of complex **1a** is coordinated by hydrogen atoms of methane molecule in a mono- or tridentate fashion. The Br(5) terminal atom of donor-acceptor complex **1b** weakly interacts with methane at either the hydrogen atom (complex **2b**) or the carbon atom (complex **3b**). The structures of the interacting fragments remain virtually unchanged; therefore no figures corresponding to these complexes are given.

Attacks of complexes **1c,d** on the hydrogen atom of methane molecule result in the barrierless formation of complexes **2c,d** (Fig. 2), respectively.

Complex **2c** corresponds to the global minimum on the PES of system II. The structure of this complex comprises two clearly seen fragments sharing the bromine atom. These are the H_3CHBr fragment similar to ion **A**, which is formed as a result of a barrierless addition of the Br^+ cation to the methane molecule, and the $Br_2 \cdot AlBr_3$ donor-acceptor complex whose structure is a combination of the structures **1c** (the bonds at the Al atom) and **1d** (the bonds at the Br(5) atom). The attack of complex **1d** on the hydrogen atom of methane molecule results in complex **2d**. Here, the geometry of the H_3CHBr fragment remains virtually unchanged as compared to that in **2c**; however, the bromine atom of this fragment is "solvated" by the $AlBr_4^-$ counterion in a tridentate fashion and the initial donor-acceptor complex **1d** is "destructed." The attacked C—H bond in complexes **2c,d** is appreciably lengthened and weakens; of course, this lengthening is much smaller than that in ion **A** formed in the $[Br^+ + CH_4]$ model system (~0.04 Å *vs.* 0.15 Å, respectively).

Complexes **1c,d** attack the carbon atom of methane molecule to give the barrierlessly formed complexes **3c,d**, respectively (see Fig. 2).

The structure of the fragments of asymmetrical complex **3c** (C_1), (the methane molecule and complex **1c**) changed only slightly, though the complexation energy is 8.8 kcal mol^{-1}. In the symmetrical complex **3d** (C_{3v}), the bromine atom carrying a rather large positive charge (0.53 au) forms a weak bond with the carbon atom of the nearly undistorted methane molecule. This bromine atom is "solvated" by the $AlBr_4^-$ counterion in a triden-

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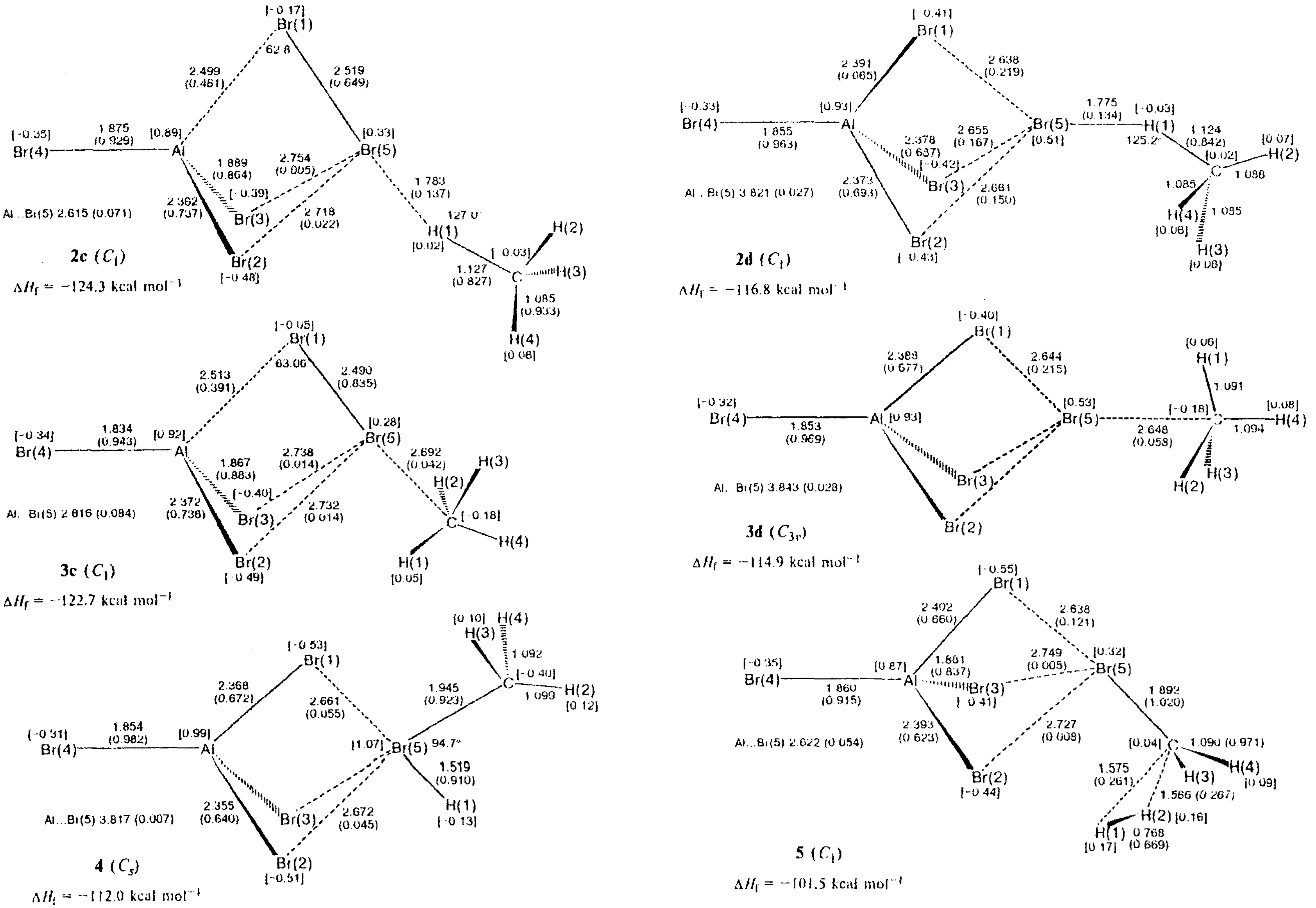
* Several local minima were also found on the PES of this system, corresponding to different configurations of the systems in which the CH_4, H_3CBr, and HBr molecules weakly interact with the aluminum bromide complexes $Br_2 \cdot AlBr_3$, $HBr \cdot AlBr_3$, and $H_3CBr \cdot AlBr_3$, respectively.



Al...Br(5) 2.615 (0.071)

2c (C_1)

$\Delta H_f = -124.3$ kcal mol^{-1}

Al...Br(5) 3.821 (0.027)

2d (C_1)

$\Delta H_f = -116.8$ kcal mol^{-1}

Al...Br(5) 2.816 (0.084)

3c (C_1)

$\Delta H_f = -122.7$ kcal mol^{-1}

Al...Br(5) 3.843 (0.028)

3d (C_{3v})

$\Delta H_f = -114.9$ kcal mol^{-1}

Al...Br(5) 3.817 (0.007)

4 (C_s)

$\Delta H_f = -112.0$ kcal mol^{-1}

Al...Br(5) 2.622 (0.054)

5 (C_1)

$\Delta H_f = -101.5$ kcal mol^{-1}

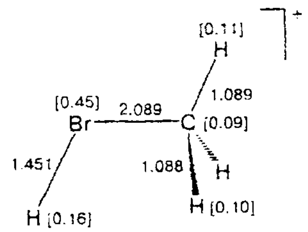
Fig. 2. Structures of complexes corresponding to local minima in the [$AlBr_5$ + CH_4] system. The bond lengths (in Å), bond angles (in degrees), bond orders (in au, figures in parentheses), and effective atomic charges (in au, figures in square brackets) are indicated.

tate fashion. Complex **3d** is characterized by virtually complete destruction of the structure of the donor-acceptor electrophile **1d**. In all three complexes **3b—d**, changes in the structure of methane molecule are insignificant, so no methane activation occurs.

Our study of the PES of system II, carried out in order to find the pathways for the formation of intermediates corresponding to the classical Olah scheme of electrophilic activation of alkanes (Scheme 1) or to the Schreiner scheme (Scheme 2), showed that neither a product of the attack on the C—H bond nor an intermediate with the 3c-2e bond between the H_2 molecule and the carbon atom are barrierlessly formed in this system.

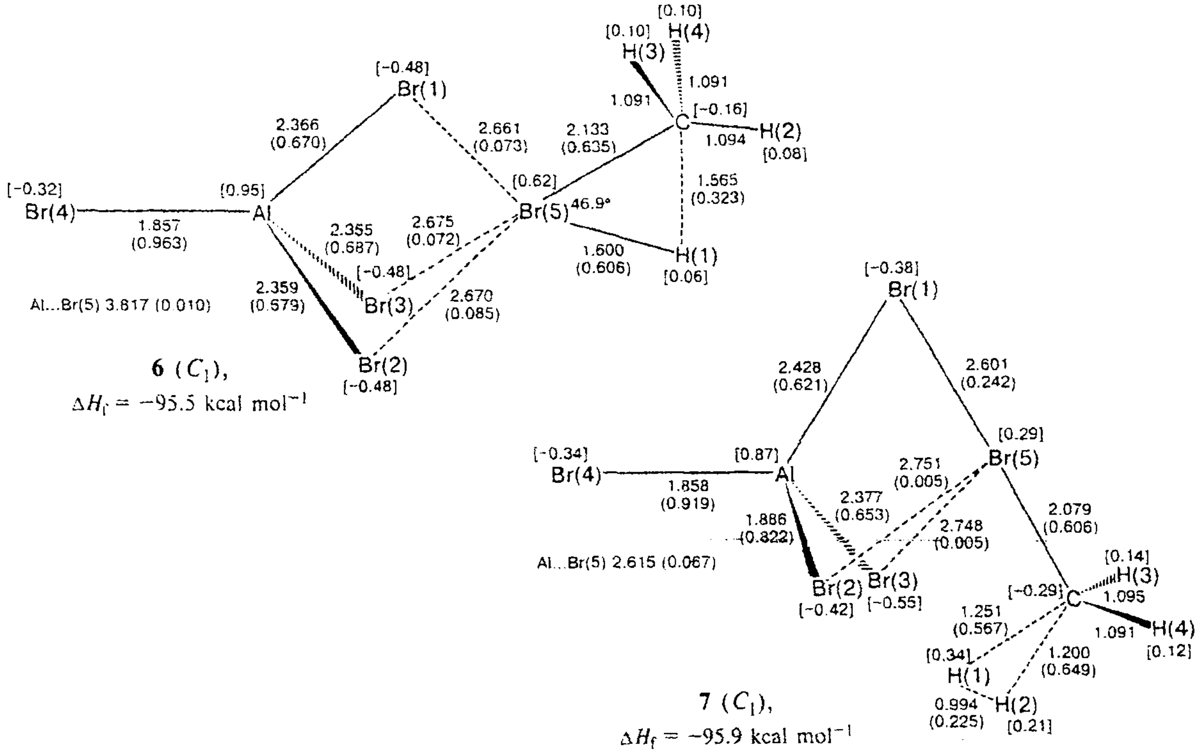
In the model system $[Br^+ + CH_4]$,[15] insertion of the bromine atom into the C—H bond of cation **A** results in the formation of bromonium ion **B** (the bond lengths are given in Å and the atomic charges are given in au in square brackets).

Scheme 4



B

In system II, this ion corresponds to complex **4** (see Fig. 2), which is the bromonium ion whose Br(5) atom is "solvated" by the $AlBr_4^-$ counterion in a tridentate fashion. As a result, the positive charge on the bromonium center increases, the bond between this center and the carbon atom strengthens, and that between this center and the hydrogen atom weakens. The distinction between system II and the model system should be mentioned. The former is characterized by high (21.3 kcal mol^{-1}) potential barrier to transition from complex **2d**, which is barrierlessly formed according to Scheme 3, to the bromonium complex **4**, whereas in the latter the formation of the bromonium ion occurs with ease (the potential barrier to transformation **A** ↔ **B** is 4 kcal mol^{-1}).[15] Transition state **6** of transformation **2d** ↔ **4** (Fig. 3), obtained from calculations along the Br(5)...C distance or the C—Br(5)—H(1) angle used as intrinsic reaction coordinate *R*, corresponds to the Olah scheme (see Scheme 1).



6 (C_1), ΔH_f = −95.5 kcal mol^{-1}

7 (C_1), ΔH_f = −95.9 kcal mol^{-1}

Fig. 3. Structures of transition states of transformations **2d** ↔ **4** (**6**) and **2c** ↔ **5** (**7**) in the $[AlBr_5 + CH_4]$ system. The bond lengths (in Å), bond angles (in degrees), bond orders (in au, figures in parentheses), and effective atomic charges (in au, figures in square brackets) are indicated.

Finally, complex **5** (see Fig. 2) was found on the PES of system II, in which the H_2 molecule forms the 3c-2e bond with the carbon atom in accordance with the Schreiner scheme (see Scheme 2). The Br(5) atom of the complex forms a strong bond with the C atom. This means that complex **5** is a donor-acceptor complex between the H_2 molecule and the CH_2Br^+ cation whose bromine atom, which carries a rather large positive charge, is "solvated" by the $AlBr_4^-$ counterion in a tridentate fashion. The position of the local minimum corresponding to complex **5** on the energy scale is much higher than those of the previously discussed minima. Therefore, the potential barrier to the formation of this complex is also high (28.4 kcal mol^{-1}). This activation energy corresponds to transition state **7** of transformation **2c** ↔ **5** (see Fig. 3).

Comparison of the PES of the model system $[Br^+ + CH_4]$ and system II showed that in both cases the attack of electrophile on the hydrogen atom of methane molecule results in the barrierless formation of corresponding complexes. Among them, there are complexes **A** and **2c,d** in which the bond between the C atom and the attacked H atom becomes lengthened and weakens. Thus, the methane molecule in these complexes is activated. Further transformations of complexes **A** and **2c,d** result in products whose structures formally correspond to the attack of electrophiles on the C—H bond or on the C atom of methane molecule in accordance with the Olah scheme (see Scheme 1) or with the Schreiner scheme (see Scheme 2), respectively. However, whereas the barriers to these transformations in the $[Br^+ + CH_4]$ model system are low, those in system II are rather high. In addition, the complexes corresponding to the attack of electrophile on the C atom of methane molecule are also formed barrierlessly in system II; however, no activation of the CH_4 molecule occurs in this case.

As should be expected, the energy differences between both systems are substantial (Fig. 4). In the model system $[Br^+ + CH_4]$, the most stable are the bromonium cation (**B**) and the Schreiner type complex $H_2C(H_2)Br^+$ (**C**) between the methylene bromide cation and H_2 molecule, *i.e.*, the species characterized by fundamental rearrangement of the methane molecule. Species formed as a result of direct attack of the cation on the hydrogen (**A**) or carbon atoms (H_4CBr^+, with C_{4v} symmetry) (**D**) of methane molecule are less energetically favorable.

After replacement of the strongest electrophile, the "naked" Br^+ cation, by electrophilic complexes $Br_2 \cdot AlBr_3$ the formation of complexes characterized by the minimum rearrangement of initial stable reagents appeared to be energetically favorable.*

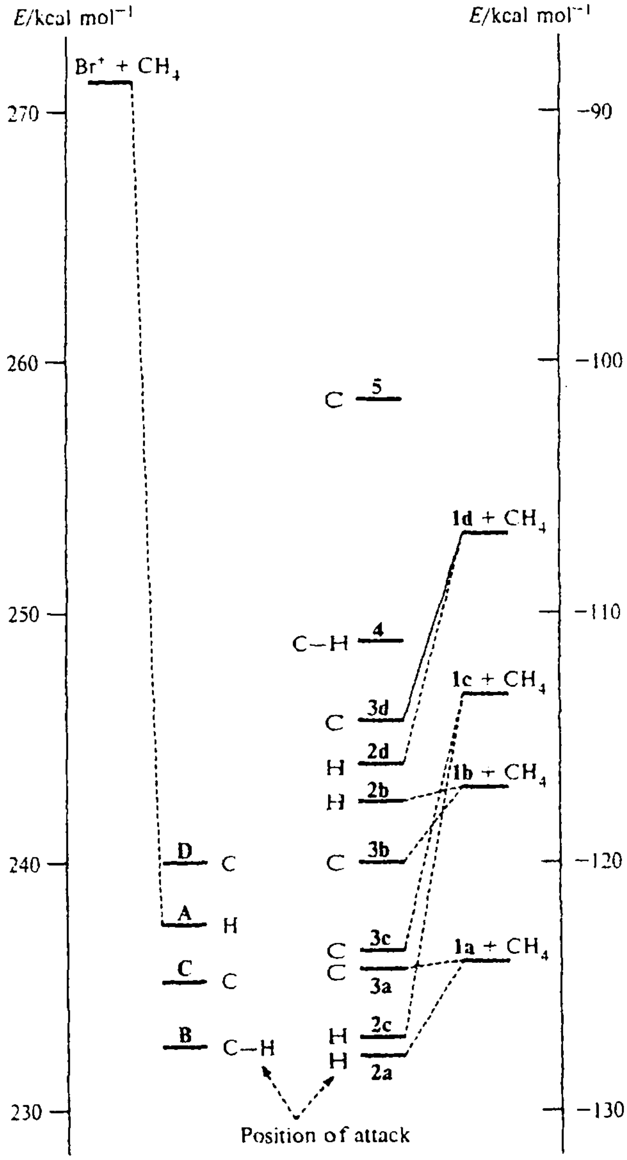


Fig. 4. Energy scheme of local minima on the PES of systems $[Br^+ + CH_4]$ (at the left) and $[AlBr_3 + CH_4]$ (at the right). Dashed lines indicate the barrierlessly formed complexes: **C** = $CH_2Br^+(H_2)$; and **D** = H_4CBr^+ (with C_{4v} symmetry).

As can be seen in Fig. 4, the $[CH_4 \cdot$ **1a**$]$ "solvates" are very stable. The complexes, which are barrierlessly formed upon the attack of the donor-acceptor complex **1b** on either a hydrogen atom (**2b**) or the carbon atom (**3b**) of methane molecule, are also among the most stable products despite weak interaction between their fragments (1.2 and 3.9 kcal mol^{-1}, respectively). The enthalpies of formation (ΔH_f) of complexes **2b** and **3b** are equal to −117.8 and −120.5 kcal mol^{-1}, respectively. More stable are only those complexes which are

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* The same principle of correspondence between the deepest local minima on the PES and the structures with minimum rearrangement of initial stable fragments was also found in *ab initio* calculations of isobutonium cations.[20]

barrierlessly formed upon the attack of complex **1c** on either a hydrogen atom (**2c**) or the carbon atom (**3c**) of methane molecule (ΔH_f −124.3 and −122.7 kcal mol^{-1}, respectively). High stability of complexes **2c** and **3c** is due not only to rather high energies of interaction between their fragments (10.4 and 8.8 kcal mol^{-1}, respectively), but also to the fact that changes in the structure of their constituent molecules are insignificant despite their interaction and therefore no considerable expenditure of energy is required.

Less stable are the structures which are barrierlessly formed upon the attack of complex **1d** on a hydrogen atom (**2d**) or the carbon atom (**3d**) of methane molecule. In these complexes, the Br(5) atom carrying a larger positive charge is "solvated" by the $AlBr_4^-$ counterion in a tridentate fashion; that is to say, destruction of donor-acceptor complex **1d** occurs as a result of its interaction with methane. As a consequence, the bromonium complex (**4**) and the Schreiner complex (**5**) appear to have the highest energies, whereas in the model system they corresponded to the most stable species. In these complexes, where the Br(5) atom carrying a large positive charge is "solvated" by the $AlBr_4^-$ counterion in a tridentate fashion, the geometry of the fragment corresponding to the attacking electrophile is also changed. However, the most important in this case is that the structure of the fragment corresponding to the methane molecule changed fundamentally.

In conclusion, mention may be made that it does not always happen that the PM3 method correctly describes complexation. However, chemical plausibility and naturalness of the results obtained indicate that the PM3 method is adequate to the problem posed. In addition, it should be emphasized that the results of our MNDO/PM3 calculations of the model system $[Br^- + CH_4]$ are in qualitative agreement with the results of *ab initio* MO LCAO calculations of the $[NO^+ + CH_4]$ system carried out using different basis sets and with inclusion of correlation corrections.[3]

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