

New Mechanisms of Alkane Activation by Superelectrophiles. MNDO/PM3 Study of Activation of Methane and Propane by Cationic Bromine-Centered Electrophiles

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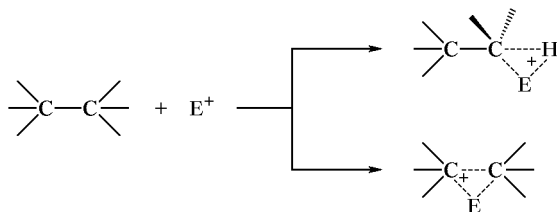
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Abstract—Fragments of the potential energy surface for the systems $C_3H_8 + Br_2 \cdot AlBr_3$, $CH_4 + CBr_3^+$, and $CH_4 + CBr_3^+ AlBr_4^-$ were simulated by the MNDO/PM3 method with a view to study the mechanisms of reactions of alkanes with new-generation superelectrophiles. Two new mechanisms were revealed for the reaction of alkanes with superelectrophiles. In the three examined systems, weakly bonded adducts are formed, which may be regarded as electrophile “solvates” with alkane molecules. Various ways of transformations of such solvates were examined. Radically new mechanisms were proposed for the bromination of methane with superelectrophiles CBr_3^+ and $CBr_3^+ AlBr_4^-$. The potential barrier to bromination is reduced to 17–25 kcal/mol due to nucleophilic assistance by lone electron pairs on the bromine atoms. By contrast, the reaction of propane with the $Br_2 \cdot AlBr_3$ complex is described in terms of the classical Olah scheme.

Since the early 1970s, electrophilic activation of alkanes has become the subject of extensive studies. The most significant contribution to these studies was made by Olah and co-workers [1–3]. The classical Olah mechanism (Scheme 1) involves attack by an electrophile E^+ on σ -C–H or σ -C–C bond of alkane with formation of a three-center two-electron (3c-2e) intermediate or transition state (TS) [1–3].

Scheme 1.



An alternative mechanism of alkane activation was proposed on the basis of nonempirical quantum-chemical study of nitrosation of alkanes (Scheme 2).

Scheme 2.



It includes attack by NO^+ cation directly at the carbon atom with synchronous formation of a 3c-2e bond between that carbon atom and H_2 quasimolecule [4, 5] (this mechanism was subjected to criticism in [3]).

While starting our theoretical studies on electrophilic activation of saturated hydrocarbons by superelectrophilic systems of new generation [6], we have examined aluminum halide complexes with halogens (inorganic superelectrophiles [7]) and polyhalomethanes (organic superelectrophiles [8]). The results of quantum-chemical calculations of the potential energy surfaces (PES) for aluminum halide complexes with polyhalomethanes [9, 10] and halogens [11, 12] showed that these systems also give rise to complexes in which one of the halogen atoms possesses a large positive charge. The formation of such complexes could be responsible for the high activity of the above systems toward alkanes. Figure 1 shows the structures of two complexes A and B [12, 13] having large positive charges on the bromine atoms. These structures have been utilized in the present study.

Our quantum-chemical study of the mechanism of reactions of alkanes with bromine-centered superelectrophilic complexes was initiated with the model

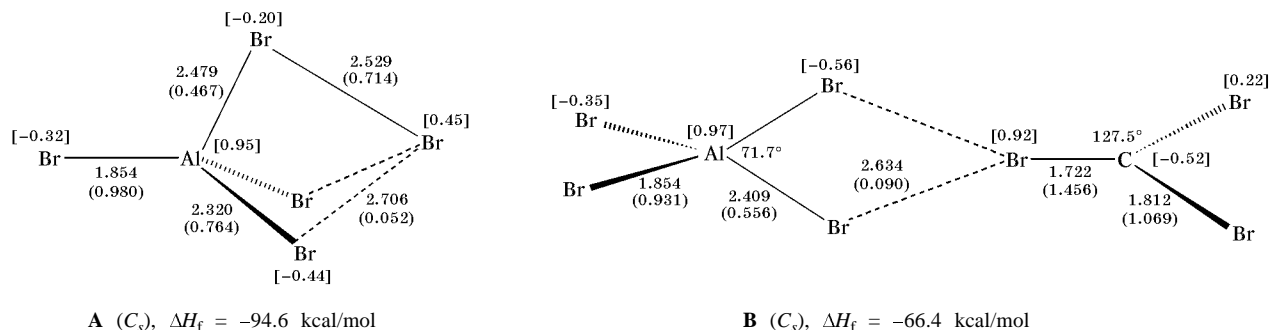
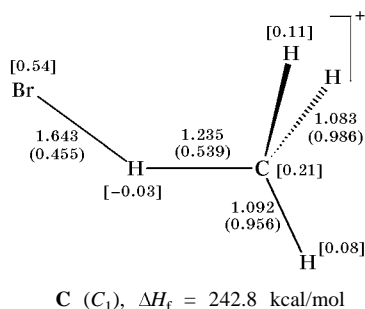


Fig. 1. Structures of complexes **A** and **B**. Hereinafter, given are bond lengths (Å), bond orders (a.u., in parentheses), and Coulson effective charges (a.u., in brackets).

system $\text{CH}_4 + \text{Br}^+$ (**I**) [14]. It was surprising that the scheme of reactions occurring in this system involves barrier-free formation of cation **C** which contains a hypervalent hydrogen atom:



Here, Br^+ ion adds to the methane hydrogen atom, thus activating the C–H bond so strongly that, while moving off, it carries away hydride ion (Scheme 3).

Scheme 3.



We have thus discovered the third possible mechanism for activation of alkanes by electrophiles. It involves attack neither on the C–H bond with formation of cyclic 3c-2e intermediate or transition state (Scheme 1) nor on the C atom with formation of 3c-2e bond with hydrogen molecule (Scheme 2), but on the hydrogen atom of the C–H bond with subsequent rupture of that bond (Scheme 3). These findings prompted us to examine the scope of application of the new mechanism of alkane activation.

While studying the system $\text{CH}_4 + \text{Br}_2 \cdot \text{AlBr}_3$ (**II**), we have found [12, 15] that activation of C–H bonds in methane upon barrier-free addition to its hydrogen atom of different isomers of the neutral $\text{Br}_2 \cdot \text{AlBr}_3$ complex is insufficient for the mechanism shown in

Scheme 3 to be operative, despite an appreciable positive charge (0.45 a.u.) on the bromine atom in one of the isomers (**A**). Further transformations of the H-complexes $\text{H}_3\text{CH} \cdot \text{BrAlBr}_4$ involve either Olah's transition state (Scheme 1) or species with a hydrogen quasimolecule (Scheme 2). The potential barriers to such transformations range from 20 to 30 kcal/mol.

The difference between the mechanisms of reactions of methane with Br^+ ion and $\text{Br}_2 \cdot \text{AlBr}_3$ complex suggests that the probability for alkane activation by electrophiles according to the new mechanism (Scheme 3) is determined by the relation between the strength of the alkane C–H bond being broken and the electrophile power. In keeping with the above assumption, study of the systems $\text{C}_3\text{H}_8 + \text{CBr}_3^+$ (**III**) and $\text{C}_3\text{H}_8 + \text{CBr}_3^+ \cdot \text{AlBr}_4^-$ (**IV**) showed [13] that hydrogen abstraction from the secondary carbon atom in propane by CBr_3^+ ion, both as a free species and as a part of neutral complex **B**, occurs as a direct transition to the superelectrophile carbon atom according to Scheme 3, i.e., without formation of cyclic 3c-2e transition state or intermediate.

In order to elucidate the scope of operation of the new mechanism of alkane activation (Scheme 3), the following questions should be answered: (1) Is the lability of the secondary C–H bond in propane sufficient for realization of Scheme 3 with $\text{Br}_2 \cdot \text{AlBr}_3$ complexes which are weaker electrophiles than $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ [6]; and (2) Are the electrophiles CBr_3^+ and $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ sufficiently powerful to abstract hydride ion from methane which is the most stable alkane. For this purpose, we performed quantum-chemical calculations of fragments of the potential energy surfaces for the systems $\text{C}_3\text{H}_8 + \text{Br}_2 \cdot \text{AlBr}_3$ (**V**), $\text{CH}_4 + \text{CBr}_3^+$ (**VI**), and $\text{CH}_4 + \text{CBr}_3^+ \cdot \text{AlBr}_4^-$ (**VII**). The calculations were performed by the MNDO/PM3 method with full optimization of geometric parameters, using PC GAMESS [16, 17], MOPAC 6.0 [18], and

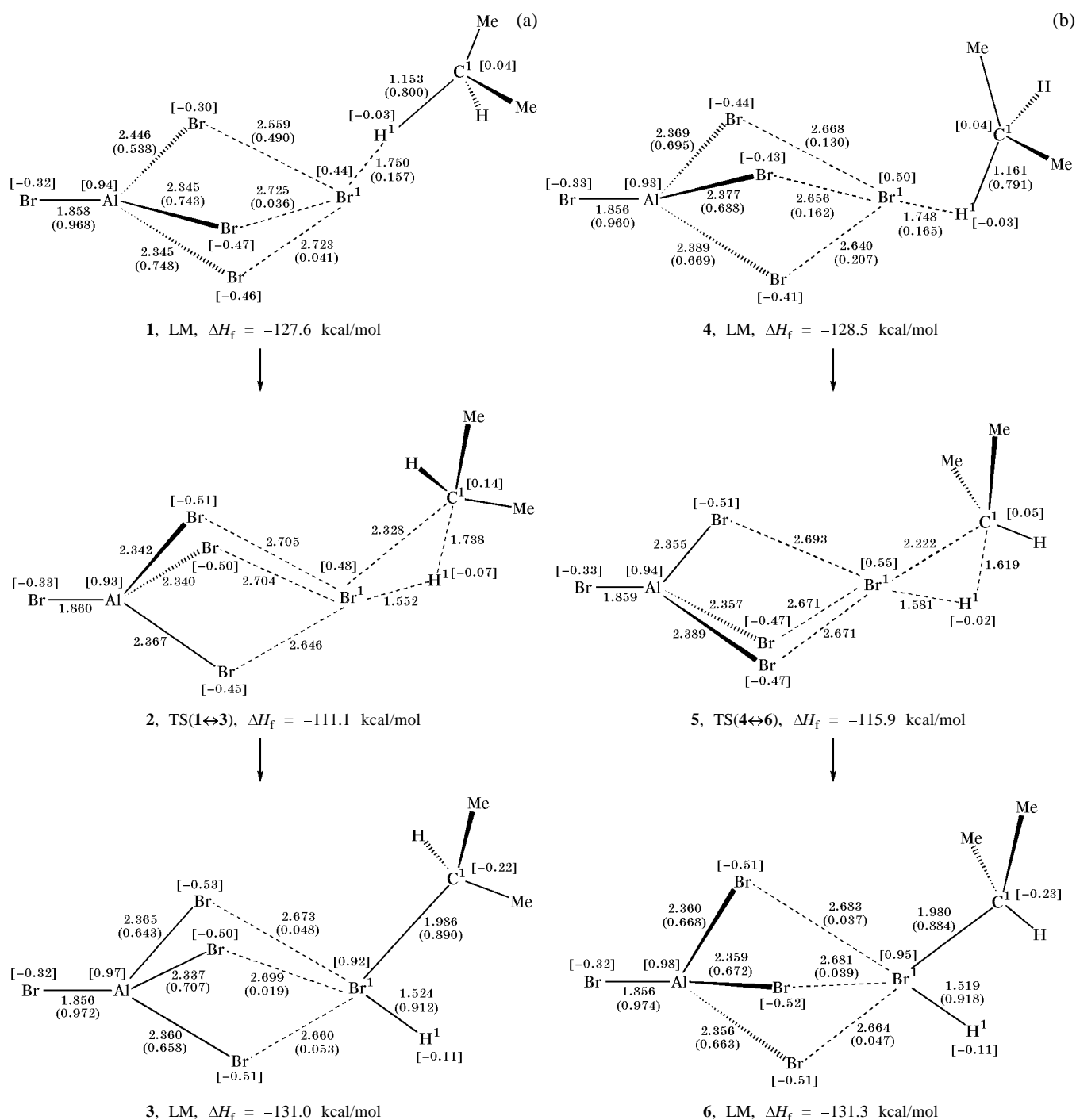


Fig. 2. Formation of bromonium complexes in the system $C_3H_8 + Br_2 \cdot AlBr_3$ (V) along the reaction coordinate (a) $R_c = [C^1 \cdots H^1]/[Br^1 \cdots H^1]$ and (b) $R_c = \angle C^1 Br^1 H^1$; LM stands for local minima, and TS, for transition states. Given are bond distances (Å), bond orders [23] (in parentheses), and Coulson effective charges (a.u., in brackets).

GAUSSIAN 94 software packages [19] on an SGI POWER CHALLENGE supercomputer server (which was installed at the Institute of Organic Chemistry, Russian Academy of Sciences; RFBR project no. 95-07-021). Stationary points on the PES were iden-

tified by the number of negative Hessian eigenvalues. The geometric and electronic structures corresponding to local minima (LM) and transition states (PS) were calculated in the UHF approximation. For all systems under study, eigenvalues of the S^2 operator were equal

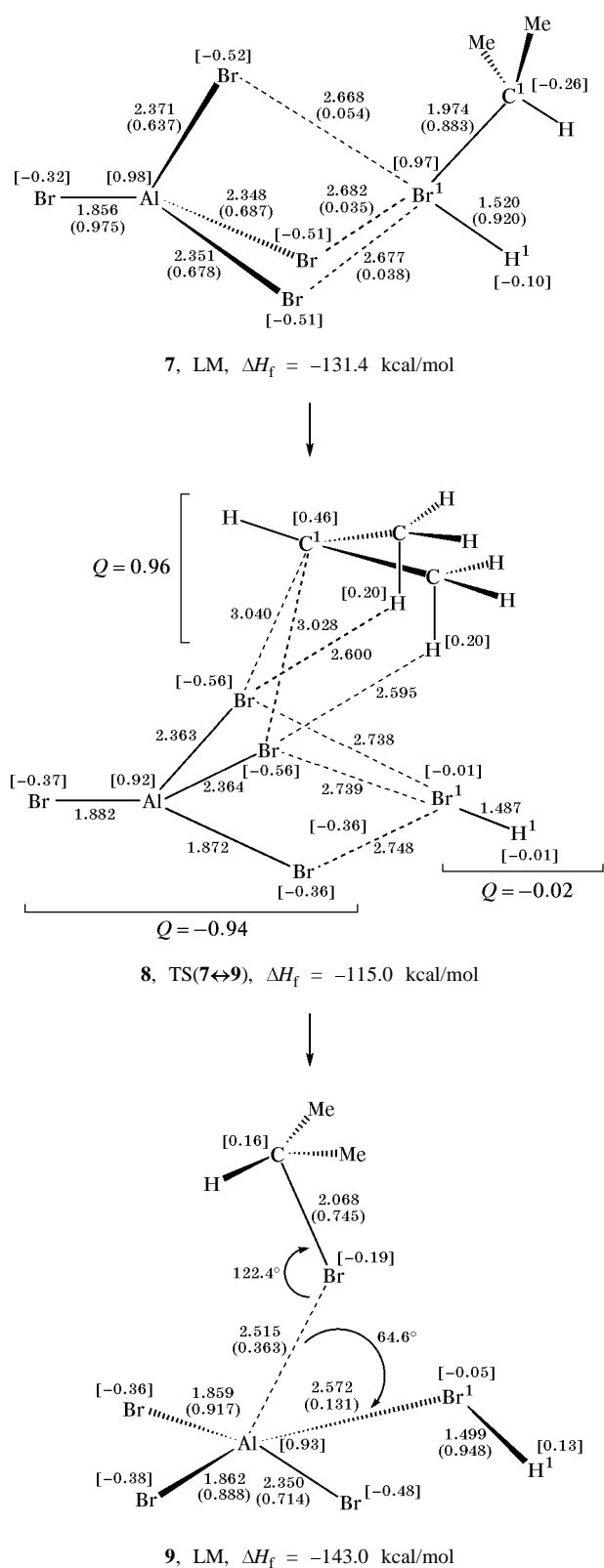


Fig. 3. Cleavage of the bromonium complex formed in system **V** along the reaction coordinate $R_c = C^1 \cdots Br^1$. For notations, see legends to Figs. 1, 2.

to zero, and the results of UHF and RHF calculations were consistent with each other. Transition states were calculated according to Schlegel [20] (PC GAMESS) and using the QST2 procedure (GAUSSIAN-94; from geometric parameters of the two states corresponding to appropriate local minima). The reverse motion (from TS to LM) was studied in the IRC (Intrinsic Reaction Coordinate) mode. Preliminary results of the calculations by the nonempirical Hartree–Fock methods and those performed in the framework of the density functional theory (DFT) (which will be the subject of our subsequent publication) were in agreement with our present results.

Mechanism of the reaction of propane with $Br_2 \cdot AlBr_3$ complexes (system V). The potential energy surface for system **V** was studied with various initial arrangement of the donor–acceptor $Br_2 \cdot AlBr_3$ complexes [12] relative to the propane molecule using a number of reaction coordinates. The potential curves corresponding to those reaction coordinates indicate barrier-free formation of weakly bonded adducts in which the electrophile is “solvated” by propane. In most cases, the subsequent variation of the reaction coordinate led to appearance on the potential curves of small barriers corresponding to transformation of one “solvate” into another. More profound transformations were revealed only for propane solvates with the most electrophilic $Br_2 \cdot AlBr_3$ donor–acceptor complex [12], namely with complex **A**. A significant contribution to the electronic state of complex **A** is that of the ionic structure in which the Br^+ cation is linked to three bromine atoms of the $AlBr_4^-$ anion. The potential curves along the reaction coordinate $R_c = Br^1 \cdots H^1$ indicate that propane-solvated complexes **A** (which are formed with no barrier) are transformed into various conformers of electrostatic complexes of bromonium ion with $AlBr_4^-$ through a fairly high barrier. As an example, Fig. 2 shows schemes corresponding to the reaction coordinates $R_c = (C^1 \cdots H^1)/(Br^1 \cdots H^1)$ (a) and $R_c = \angle C^1 Br^1 H^1$ (b). It is seen (Fig. 2a) that solvate **1** is transformed into bromonium complex **3** through transition state **2** which is typical of the Olah scheme. The potential barrier to this transformation is 16.5 kcal/mol. Figure 2b illustrates the transformation of another solvate **4** into bromonium complex **6** through transition state **5**. The latter is also typical of the Olah scheme. The potential barrier is slightly lower and is equal to 12.6 kcal/mol.

The subsequent course of electrophilic bromination of propane with complex **A** was traced by examining the potential curves for abstraction of hydrogen bromide from bromonium complexes. After passing

a point corresponding to TS, the energy sharply decreases due to formation of five-coordinate complexes of aluminum bromide with PrBr and HBr. Hydrogen bromide thus leaves the bromonium complex, and the remaining isopropyl cation takes up one bromine atom from the AlBr_4^- anion. Further increase in the distance between the C^1 atom in propyl bromide and Br^1 in hydrogen bromide (which no longer affects the reaction under study) is accompanied by transitions between different conformers of the $\text{HBr} \cdot \text{AlBr}_3 \cdot \text{BrC}_3\text{H}_7$ complexes. Figure 3 shows the main steps of this process which involves bromonium complex **7**, transition state **8** for abstraction of hydrogen bromide, and complex **9** formed by propyl bromide, hydrogen bromide, and aluminum bromide. As follows from Fig. 3, the transition state is characterized by electrostatic interaction between two bromine atoms of the AlBr_4^- anion and isopropyl cation. This interaction is contributed mainly by the secondary carbon atom of C_3H_7^+ and two methyl hydrogen atoms oriented toward the anion. The potential barrier is not high (16.4 kcal/mol) due to electrostatic stabilization of the transition state. A general energy diagram for the electrophilic bromination of propane with complex **A** is shown in Fig. 4.

Mechanism of the reaction of methane with CBr_3^+ (system VI). Stationary points on the potential curves describing the approach of methane to CBr_3^+ ion (for results of quantum-chemical calculations of CBr_3^+ , see [9, 21, 22]) correspond to numerous solvates whose formation involves no barrier and transition states for their interconversions. Further decrease of the reaction coordinate (shortening of the distance between the reactants) is accompanied by continuous increase in energy. Extension of the distance between the bromine atom and methane carbon atom ($R_c = \text{Br}^1 \dots \text{C}^1$) in the solvates does not lead to rupture of the C–H bond, as was the case in the reaction of methane with Br^+ ion.

More profound transformation of methane occurs only along the reaction coordinate corresponding to rupture of the methane C–H bond. Extension of the $\text{C}^1 \dots \text{H}^1$ distance in the solvate leads to formation of bromonium complex. Figure 5 shows the structure of transition state **11** between the initial H-complex **10** and bromonium complex **12**. It is seen that hydride ion abstracted from the methane molecule in the transition state is already coordinated to the carbon atom of CBr_3^+ . Rotation of the latter leads to shortening of the distance between one of the bromine atoms and methane carbon atom and formation of a bond between these atoms. The transition state is quite different from Olah's transition state: It is neither

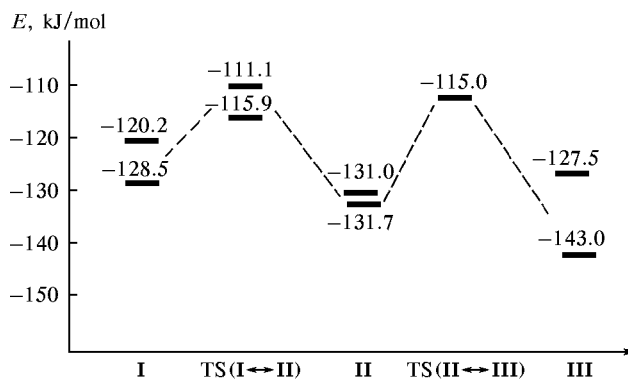
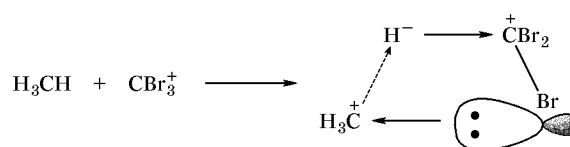


Fig. 4. Generalized energy diagram for the bromination of propane with complex **A** ($\text{Br}_2 \cdot \text{AlBr}_3$). Given are energy intervals for solvates **I**, bromonium complexes **II**, AlBr_3 complexes **III** with HBr and $\text{C}_3\text{H}_7\text{Br}$, and the corresponding transition states $\text{TS}(\text{I} \leftrightarrow \text{II})$ and $\text{TS}(\text{II} \leftrightarrow \text{III})$.

two-electron nor three-center. Initially, it was localized in the SADPOINT mode from the maximum on the potential energy curve, and then by the QST2 procedure for the transition from H-complex **10** to final bromonium complex **12**. Thus the reaction of methane with CBr_3^+ ion, leading to the bromonium complex $[\text{H}_3\text{CBrCBr}_2\text{H}]^+$, follows Scheme 4. This mechanism differs from those shown in Schemes 1–3 and is characterized by nucleophilic assistance of lone electron pairs of bromine in the CBr_3^+ ion to hydride ion transfer from the methane molecule.

Scheme 4.



Further transformations of bromonium complex **12** were simulated by breaking the bond between the positively charged bromine atom and the dibromomethyl group (Fig. 5). As a result, bromomethane solvate of HCBBr_2^+ ion (**14**) is formed. Transition state **13** which mediates the transition from **12** and **14** is linear.

It should be noted that, while looking for transition state between methane solvate $\text{CH}_4 \cdot \text{CBr}_3^+$ (**15**) and bromomethane solvate $\text{CH}_3\text{Br} \cdot \text{HCBBr}_2^+$ (**17**) by the QST2 procedure (Fig. 6), we have localized transition state **16** which resembles those typical of the Olah scheme (though such interpretation is somewhat strained, for the C–H bond in the three-membered $\text{C}^1\text{H}^1\text{Br}^1$ ring is broken almost completely: the

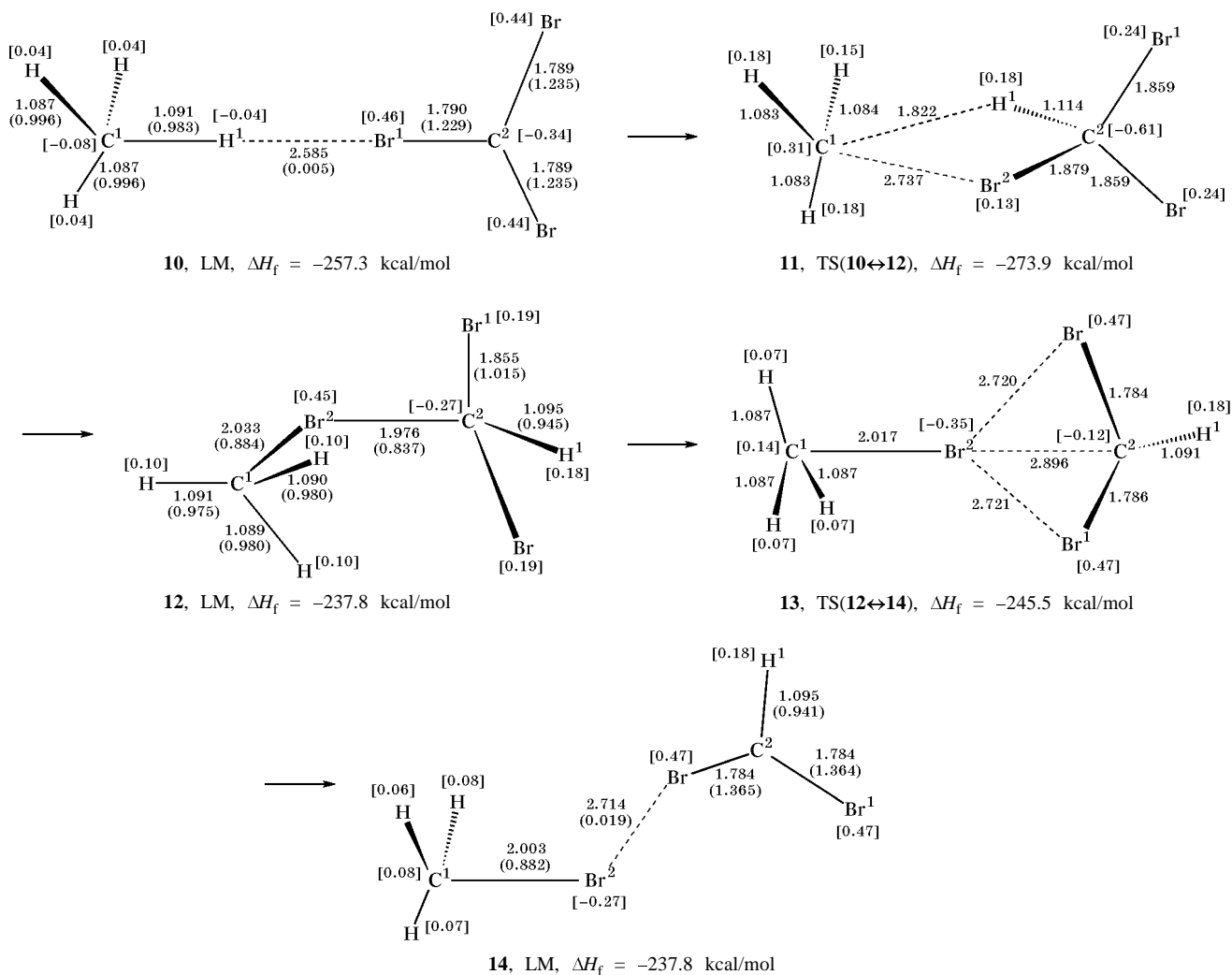


Fig. 5. Alternative path for the bromination of methane with CBr_3^+ ion.

$\text{C}^1 \cdots \text{H}^1$ distance is about 2 rather than 1 Å). However, this transition state is characterized by an extremely high potential barrier of 63.3 kcal/mol, whereas the above alternative route through bromonium complex involves relatively low barriers: 16.6 kcal/mol for formation and 7.7 kcal/mol for decomposition of the bromonium complex.

Mechanism of the reaction of methane with the $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ complex (system VII). The reaction of methane with $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ [13] was examined by the potential curves corresponding to approach of the methane molecule to the Br^1 atom (cationic center of complex **B**), C^2 , and bromine atoms of the AlBr_4^- ion. The distance to both H^1 and C^1 was varied. We thus observed only formation (and sometimes interconversions) of numerous solvates. More essential transformations were revealed along the reaction coordinate $R_c = \text{C}^1 \cdots \text{H}^1$. Extension of the methane C–H bond

in its solvates with complex **B** (which are formed with no barrier) leads in all cases to a high-energy plateau which lies 25–35 kcal/mol above the solvate energy level. Further on, the energy falls down to the region corresponding to various conformers of the bromoform adducts with donor–acceptor complexes of bromomethane with aluminum bromide. In order to refine the structures of transition states we examined the potential curve along the reaction coordinate $R_c = (\text{C}^1 \cdots \text{H}^1)/(\text{C}^2 \cdots \text{H}^1)$ in the energy plateau region and localized transition state **19** between solvate **18** and adduct **20** (Fig. 7). This transition state is characterized by almost complete hydride ion transfer from the methane molecule to the cationic fragment CBr_3^+ of complex **B** with formation of bromoform; here, the formation of bromomethane begins. Transition state **19** is an electrostatically stabilized cyclic transition state with charge transfer (Scheme 5). Elimination of

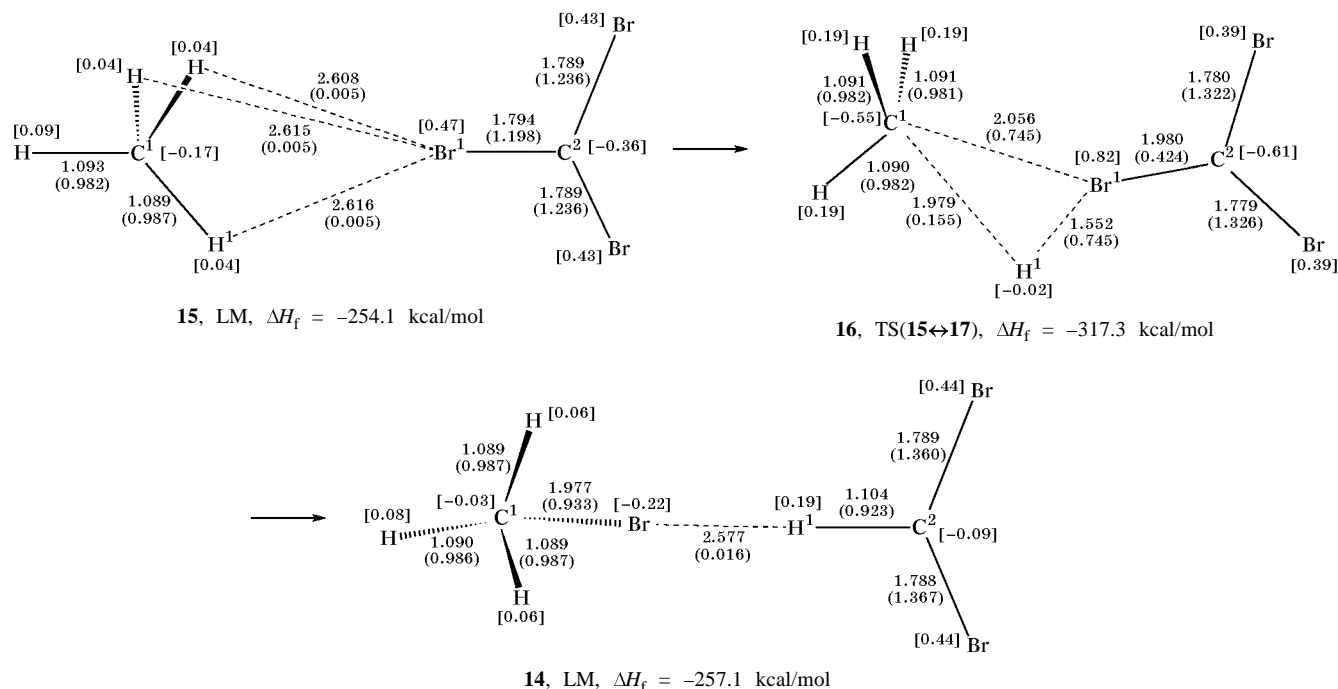
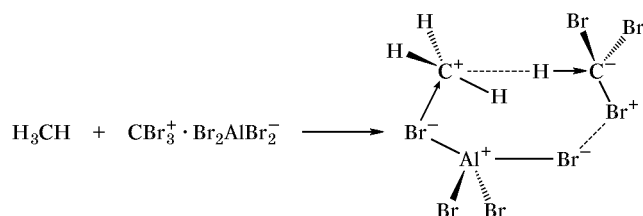


Fig. 6. Bromination of methane with CBr_3^+ ion.

hydride ion from methane and its transfer to the carbon atom of the electrophile is facilitated due to nucleophilic assistance by lone electron pairs of bromine in the anionic fragment. The height of the potential barrier is 24.6 kcal/mol, and such transition state has no analogies in the known schemes for electrophilic activation of alkanes.

Scheme 5.



Thus, in keeping with the high strength of the C–H bond in methane, its bromination according to Olah, even with such a powerful model electrophile as CBr_3^+ , requires extremely high energy of activation (63.3 kcal/mol). Nevertheless, the bromination of methane becomes possible due to nucleophilic assistance by lone electron pairs on the bromine atoms in CBr_3^+ and $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$. As a result, the potential barrier is reduced to quite acceptable values of 16.6 and 24.6 kcal/mol, respectively. The bromination of methane with CBr_3^+ follows an alternative path through formation of bromonium complex. In the

transition state, hydride ion transfer from the methane molecule to CBr_3^+ and attack by lone electron pair of bromine on the cationic methane carbon atom occur simultaneously (Scheme 4). The transition state for rupture of the C–Br bond in the bromonium complex is linear. Nucleophilic assistance for activation of methane by neutral superelectrophilic complex **B** ($\text{CBr}_3^+ \cdot \text{AlBr}_4^-$) involves electrostatically stabilized cyclic transition state with charge transfer (Scheme 5).

As concerns propane, its reactions with CBr_3^+ and $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ were shown by us previously [13] to follow Scheme 3, while the reaction with a weaker electrophile, $\text{Br}_2 \cdot \text{AlBr}_3$ is described by the Olah mechanism (Scheme 1). The results of our study of the mechanisms of alkane activation by superelectrophiles of new generation are summarized in table.

Apart from transition states TS-1, TS-2, and TS-3, which correspond to Schemes 1–3, table includes

Transition states^a in reactions of methane and propane with superelectrophiles

| Alkane | Br^+ | AlBr_5 | CBr_3^+ | $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ |
|------------------------|-------------------|-----------------|------------------|--|
| CH_4 | TS-3 | TS-1, TS-2 | TS-4 | TS-5 |
| C_3H_8 | TS-3 ^b | TS-1 | TS-3 | TS-3 |

^a Transition state numbering corresponds to Schemes 1–5.

^b Confirmed by the calculation.

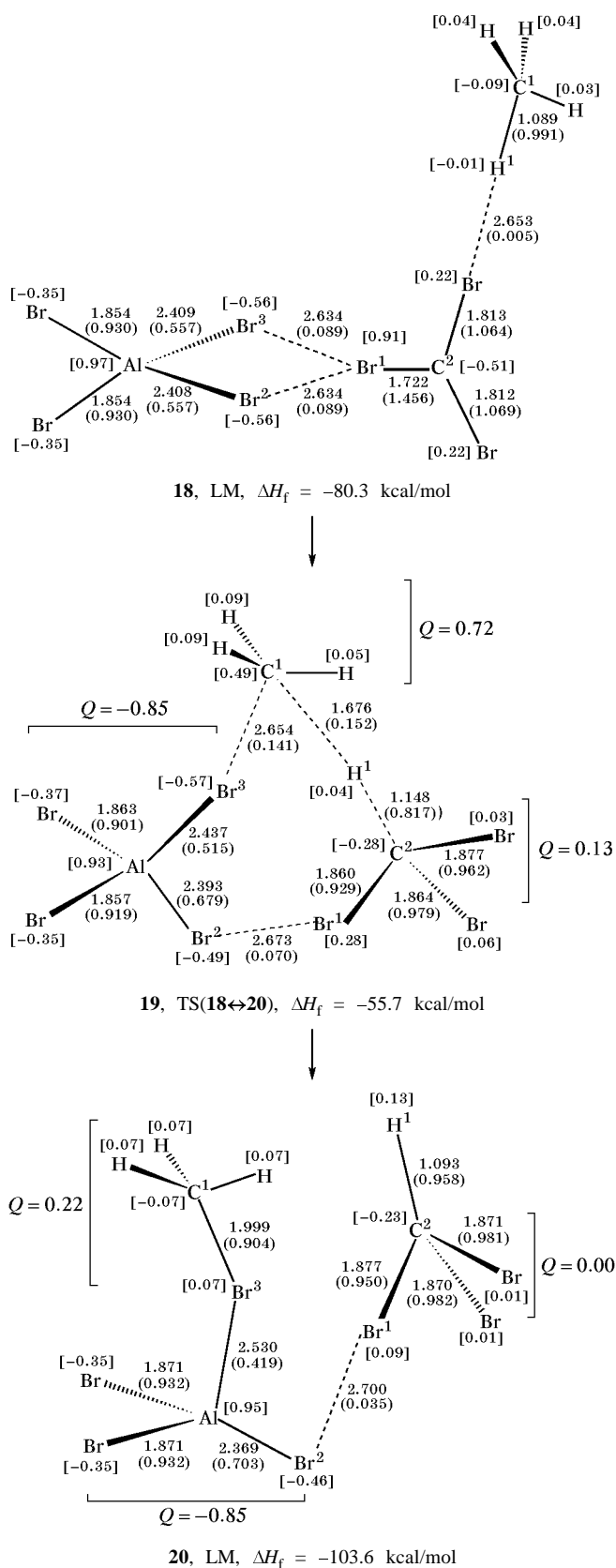


Fig. 7. Bromination of methane with $\text{CBr}_3^+ \cdot \text{AlBr}_4^-$ (**B**).

transition state TS-4 for the formation of bromonium complex, in which hydride ion transfer from methane to CBr_3^+ is accompanied by formation of a bond between bromine atom of the latter and methane carbon atom. Also, cyclic charge-transfer transition state TS-5 is given for the bromination of methane with super-electrophilic complex **B**. The data in table suggest that alkanes are capable of reacting with electrophiles via different paths, depending on the energy required in each particular case. Provided that it is profitable, electrophile attacks an alkane molecule at the C–H bond (Scheme 1); in other cases, attack on the carbon (Scheme 2) or hydrogen atom (Scheme 3) may be more favorable. If lone electron pair of bromine appears spatially close to the emerging cationic center as a result of simple rotation of the cationic fragment (Scheme 4) or, which is even better, lone electron pair resides on the nearby bromine atom possessing a negative charge (Scheme 5), two new mechanisms involving nucleophilic assistance become operative.

Thus our conclusions disrupt the exclusive position (for as long as 30 years) of the classical Olah mechanism of alkane activation. This mechanism was convincingly proved for protolytic cleavage of alkanes and was then a new stage in the theoretical organic chemistry. The results of our study on the mechanism of reactions of methane and propane with super-electrophiles of new generation indicate that other ways of alkane activation by electrophiles are also possible.

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