Nucleophilic Assistance in Methane Activation by Superelectrophiles with Halogen-Centered Cationic Sites

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Abstract—Simulation of fragments of potential energy surface for systems $CH_4 + CBr_3^+$, $CH_4 + CBr_3^+AlBr_4^-$, $CH_4 + CCl_3^+AlCl_4^-$, and $CH_4 + CCl_3^+Al_2Cl_7^-$ was performed by DFT-B3LYP and DFT-PBE methods. The important role of nucleophilic assistance in methane halogenation by these superelectrophiles was confirmed. These reactions occur with a synchronous hydride transfer from methane to the electrophile within the cyclic transition states in linear C–H–C fragment of the rings and a generation of a C–Hlg bond between the carbon atom of the arising methyl group and the halogen atom of the electrophile. The nucleophilic assistance from the unshared electron pair of this halogen atom provides the lowering of the potential barriers to methane halogenation by complexes $CBr_3^+AlBr_4^-$, $CCl_3^+AlCl_4^-$, and $CCl_3^+Al_2Cl_7^-$ to the values of the order of 20 kcal mol^{-1}. These essential features of the mechanism of methane halogenation are independent of the halogen nature and are retained on going from the model electrophiles to the real ones.

One of the fundamental problems of organic chemistry is the involvement of alkanes into selective transformations. The conception of alkanes passivity was rejected in the beginning of nineteen seventies when nontraditional systems were discovered capable of alkanes activation under mild conditions [1–4]. The most significant contribution into the discovery of alkanes cleavage effected by protic superacids belongs to Olah [5–7]. He also put forward the classic mechanism of electrophilic reactions of alkanes involving an attack of electrophile E$^+$ on C–H or C–C σ-bonds of alkane with formation of a cyclic three-center two-electron (3c-2e) intermediate or transition state [5–7] (Scheme 1).

Scheme 1.

Scheme 2.

$$CH_4 + NO^+ \rightarrow [H_2C(HH)NO]^+$$
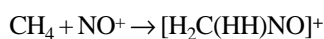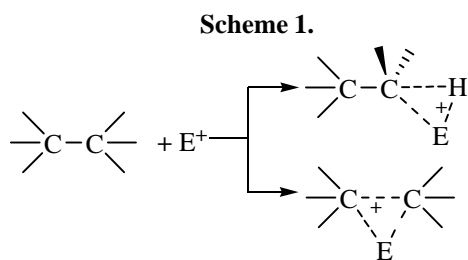
It was shown later that Olah scheme was not universal, and the alkanes reactions could also occur as a result of electrophilic attack directly of C or H atoms.

For instance, with electrophile attack on the C atom of alkane starts the alkanes oxidation with water oxide (H_2O–O) [8] and alkanes hydroxylation with hydroperoxonium cation (H_2O–OH$^+$) [9], and also insertion of carbenes into alkanes [10]. Bach et al. [8–10] succeeded in the framework of a model of frontier orbitals to predict the stereospecificity and stereoselectivity of insertions into the C–H bond of alkanes of electrophile under consideration. The systems studied were characteristically featured by the presence of an unshared electron pair in the attacking electrophile. The electrophile attack on the C atom of alkane entailed a synchronous transfer of a hydrogen of the alkane to this unshared pair. This qualitative pattern was confirmed by calculations of a high level.

Quantum-chemical ab initio calculations of alkanes nitrosation revealed that NO$^+$ cation attacked not the C–H bond of alkane but directly its carbon atom [11, 12] forming a three-center two-electron bond of this atom with a hydrogen quasimolecule (Schreiner mechanism) (Scheme 2).

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Olah et al. [7] doubted that the new mechanism found in [11] was of a general character, but they confirmed the results of calculations.

The gas-phase reactions of alkanes with BH_2^+ cation also start with attack on C atom [13].

Another mechanism also was proved involving an electrophilic attack on H atom resulting in formation of linear $3c$-$2e$ bonds with a hypervalent hydrogen. A suggestion was made already in 'sixties [14] on probable formation of C–H–C bonds in the course of electrophilic reactions of alkanes. To the end of 'seventies first experimental proofs appeared (by means of NMR spectroscopy) of the existence of linear $3c$-$2e$ bonds with hypervalent hydrogen in carbocations [15] (see also review [16] and references therein). In 'nineties Boronat et al. investigating the mechanism of hydride transfer* between alkanes and carbenium cations with the use of high-level quantum chemical methods found [17] that these reactions proceeded through stable intermediate complexes where the alkyls were linked with a linear $3c$-$2e$ C–H–C bond with a hypervalent hydrogen atom.

Boronat et al. also showed [18] that not only hydride transfer but also such acid-catalyzed reactions of hydrocarbons as disproportionation, dehydrogenation, and alkylation occurred through the intramolecular transformations of the same intermediate complexes. Note that the main qualitative characteristics of alkane complexes with carbenium cations R–H–R ⌉⁺ (R = Me, Et, i-Pr, t-Bu) calculated by Sorensen et al. [19] applying semiempirical MINDO/3 procedure coincided with the characteristics of the same type complexes obtained in [17].

Investigating by means of MNDO/PM3 method mechanism of alkane reactions with electrophiles containing halogen-centered cationic sites [20–25] we also established [23] the formation of a linear fragment C–H–C in the transition state of the hydride transfer from the methylene group of propane to electrophiles CBr_3^+ and $CBr_3^+AlBr_4^-$.

Yet in the our first study of this series we found a formation of a linear $3c$-$2e$ C–H–Br bond [20]. The model singlet cation Br^+ on adding to H atom of methane formed a linear $3c$-$2e$ C–H–Br bond, and on withdrawing from methane Br atom carried along the hydride ion (Scheme 3).

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* To be presise, the reaction of hydride transfer is so called because of its result.

Scheme 3.

$$CH_4 + Br^+ \rightarrow H_3CHBr \rceil^+ \rightarrow H_3C^+ + HBr$$

However this result turned out to be wrong in calculations carried out by the methods of higher level (DFT-PBE, DFT-B3LYB, and HF) which showed that the system $CH_4 + Br^+$ transferred into the final $CH_3BrH \rceil^+$ bromonium barrier-less. Linear $3c$-$2e$ C–H–Hlg bonds were found in studies of Schreiner and Fokin et al. dedicated to dichotomy of synchronous hydride transfer and one-electron transfer (see, e.g., [26–28] and references therein). These studies considered theoretically alkanes reactions with electrophiles possessing weak electrophilic and strong oxidative properties. In particular, there was established the formation of linear $3c$-$2e$ C–H–Hlg bonds in the transition states of alkanes halogenation [27]. Thus as should be expected the electrophile can both attack alkenes at C–H and C–C bonds forming a cyclic $3c$-$2e$ transition state, and also directly react with carbon and hydrogen of these bonds.

Moreover, depending on particular circumstances the other changes in the course of reaction between alkanes and electrophiles are also possible. We found it investigating a reaction of methane with CBr_3^+ cation and $CBr_3^+AlBr_4^-$ cation complex [24, 25]. Due to the high strength of the C–H bond in the most passive among alkanes, methane, its bromination along Olah scheme even with such powerful electrophile as CBr_3^+ requires enormously high activation energy (63.3 kcal mol⁻¹) [24]. However it proved that in reaction of methane with CBr_3^+ cation the electrophile itself can simultaneously fulfil two functions: traditional of an electrophile and nontraditional of nucleophilic assistance. Thus methane bromination becomes possible owing to the nucleophilic assistance of unshared pairs belonging to bromine in electrophiles CBr_3^+ and $CBr_3^+AlBr_4^-$, which leads to lowering of the potential barriers of this reaction to quite suitable values.

Reaction of CBr_3^+ cation with methane starts by formation of its "solvate". On increasing the C···H distance in this "solvate" a hydrogen of methane is transferred to the carbon of the CBr_3^+ fragment which turns therewith so that Br atom approaches the C atom of methane. The interaction of the unshared pair of this bromine atom with C atom of the arising methyl group decreases the potential barrier of the reaction. Schematic representation of the formerly unknown $4c$-$4e$ transition state of the reaction is shown in Scheme 4.

Scheme 4.

$$H_3CH + CBr_3^+ \longrightarrow$$
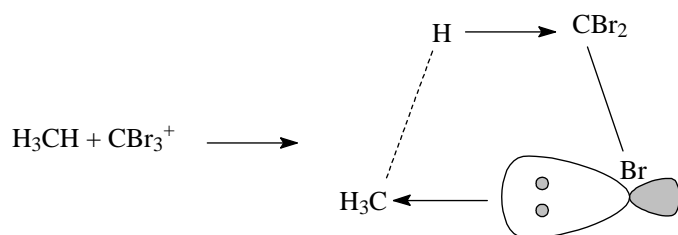
The reaction of methane with overall neutral complex $CBr_3^+AlBr_4^-$ also begins with a "solvate" formation. The departure of H atom from methane entails the approach of the incipient methyl group to the more conveniently situated and more negatively charged Br atom of electrophile linked to Al. The emerging cyclic transition state (Scheme 5) is stabilized by the nucleophilic assistance of the unshared electron pair of this Br atom.

Scheme 5.

$$H_3CH + CBr_3^+AlBr_4^- \longrightarrow$$
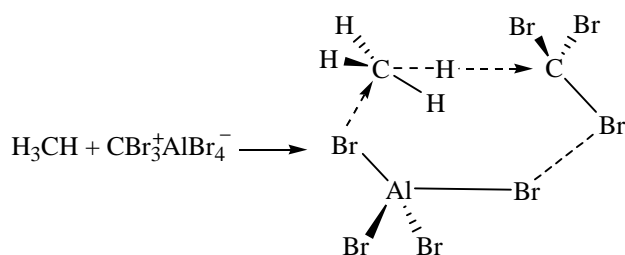
Electrophilic reactions where the attacking atom of the electrophile also had an unshared electron pair were studied in [8–10], and these reactions were also found to occur with nucleophilic assistance. However this nucleophilic assistance had different character. In these reactions the formation of 5-coordinated carbon atom resulted in increased proton lability of the hydrogen of C–H bond. The interaction with this hydrogen of the atom in the electrophile bearing the unshared pair facilitated the rupture of C–H bond. The reactions involve the electro-phile attack on the C atom, and nucleophilic assistance is directed to H atom, whereas in the reactions we investigate the nucleophilic assistance is directed to the C atom of alkane facilitating the hydride transfer.

Inasmuch as the results obtained in the framework of MNDO/PM3 procedure were significant and nontrivial they required confirmation by the quantum chemical methods of a higher level. It was also necessary to elucidate that the nucleophilic assistance to the electrophilic reactions by the unshared electron pairs of bromine was not inherent only to bromine but was also common property of all halogens. Besides in the systems under

our study only model electrophiles have been considered up till now. We should demonstrate that our results were valid also on going from model electrophiles to electrophiles which did not require very much energy to cause the dissociation of the aluminum halide dimer and therefore actually formed in the real reaction medium.

This study refines and generalizes the previously obtained results by applying quantum-chemical methods of a higher level. To this end calculations by DFT-B3LYP and DFT-PBE methods for fragments of potential energy surface (PES) of systems $CH_4 + CBr_3^+$ (**A**), $CH_4 + CBr_3^+AlBr_4^-$ (**B**), $CH_4 + CCl_3^+AlCl_4^-$ (**C**), and $CH_4 + CClr_3^+Al_2Cl_7^-$ (**D**) were performed.

The calculations were performed by DFT method in the form of generalized gradient expansion with the use of exchange-correlation potential DFT-PBE [29] and DFT-B3LYP approximation [30, 31] according to software PRIRODA-110 [32] and GAUSSIAN-94 [33] (on a supercomputer server SGI POWER CHALLENGE installed owing to the grant of the Russian Foundation for Basic Research no. 95-07-2021 in the Institute of Organic Chemistry of the Russian Academy of Sciences). Three-exponent basis was applied in the calculations by DFT-PBE method, and basis 6-31G(d), by DFT-B3LYP procedure.

A complete optimization of the geometric parameters of the systems under study was carried out. The character of stationary points was evaluated by the number of negative eigenvalues of Hessian. The geometry and electronic structure of states corresponding to local minima (LM) and transition states (TS) on PES were calculated in UHF approximation. The calculation of TS were performed using procedures QST2 and QST3 (GAUSSIAN-94) according to the geometric parameters of two states corresponding to local minima on PES whose reciprocal transition was under consideration. The search for TS by PRIRODA software was done after preliminary scanning along some possible reaction coordinates.

Thermodynamic characteristics of the reactions under study were evaluated by total energies both disregarding the zero nuclear vibrations and with accounting for them (we present the latter values).

Methane reactions with CBr_3^+ cation (system A). This reaction was calculated by DFT-B3LYB and DFT-PBE methods. On approaching CH_4 and CBr_3^+ "solvate" **A1** formed (Fig. 1). Further decreasing the distance $C^1 \cdots C^2$ entails constant energy growth. Analogous situation corresponds to the decrease in the distances

$H^1{\cdots}C^1$ or $Br^1{\cdots}C^2$. Therefore these parameters cannot be used as reaction coordinates in system **A.** Taking as reaction coordinate the ratio of distances $(Br^1{\cdots}C^2)/(H^1{\cdots}C^2)$ we obtained a smooth potential curve (PC) for the energy variation on going from structure **A1** through a maximum into a minimum corresponding to bromonium structure $H_3CBrCBr_2H]^+$ (**A3**). The geometry of the structure corresponding to the maximum of PC was refined with the use of GAMESS program in the SADPOINT mode. As a result we obtained the TS structure **A2**. Structures **A1**, **A2**, and **A3** are represented in Fig. 1 (all the data given in figures are obtained by DFT-B3LYB method). As seen from the data in Fig. 1, the hydrogen departing from methane in the transition state is already coordinated to C^1 atom in CBr_3^+ cation, whereas the approach of Br^1 atom of a CBr_3^+ cation to C atom of methane provides a possibility to the latter for

interaction with the unshared pair of the closely located Br (the $Br^1{\cdots}C^2$ distance in the transition state is less than the sum of van der Waals radii of Br and C atoms). The generated cyclic planar transition state is strongly distinct from the transition state suggested by Olah since it is four-electron instead of two-electron, and four-centered instead of three-centered. The result obtained we tested by DFT/B3LYP method using QST2 procedure of GAUSSIAN-94 program: from structures **A1** and **A3** was found the same structure **A2**.

Thus methane reaction with CBr_3^+ cation leading to the formation of bromonium $H_3CBrCBr_2H]^+$ proceeds in keeping with Scheme 4.

The results of calculations of the same reaction by DFT-PBE method confirmed (both qualitatively and quantitatively) the picture described. Both calculation
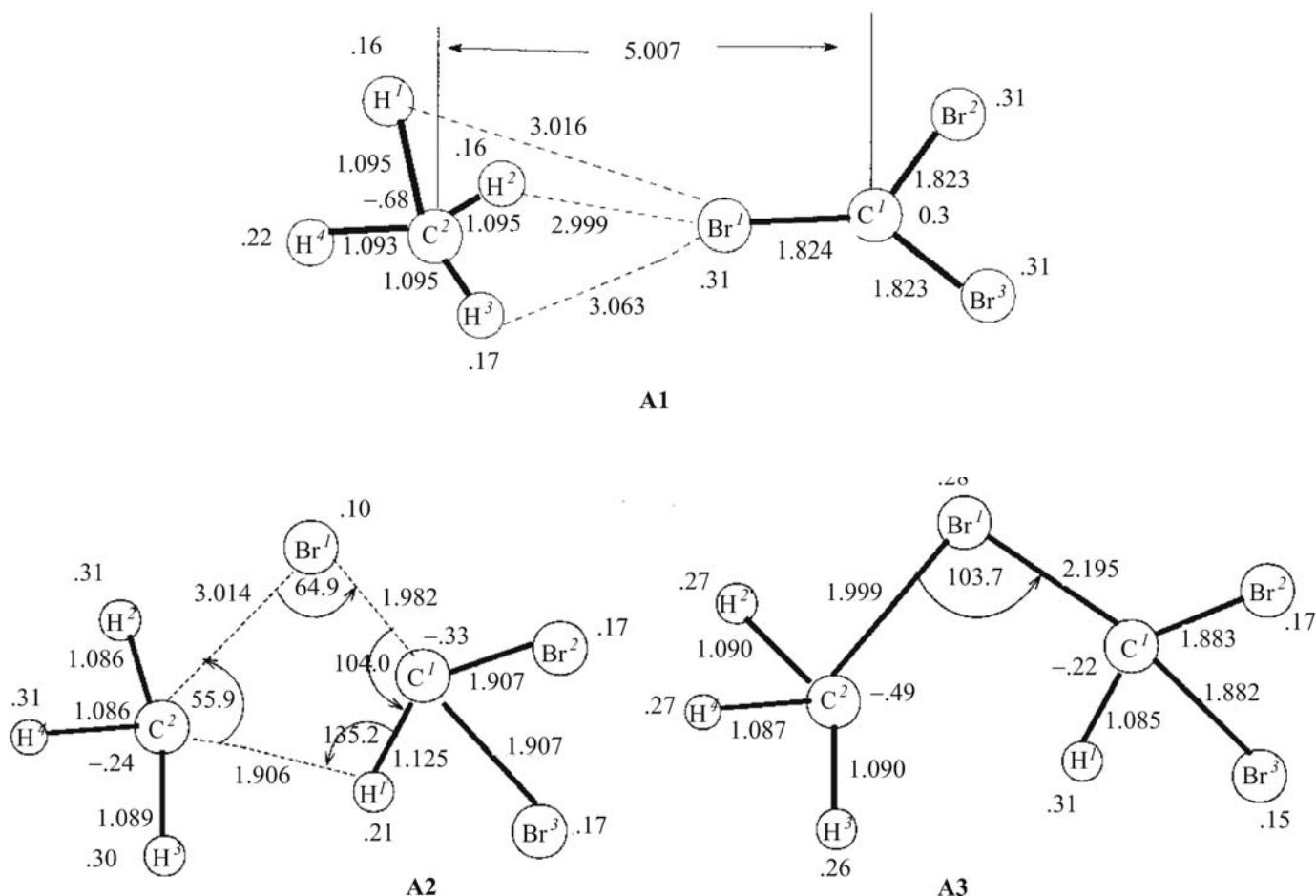

Fig. 1. Methane reaction with CBr_3^+ cation. Structures of initial solvate **A1**, reaction product **A3**, and transition state **A2**. Here and on other figures are given some distances, bond lengths (Å), and effective charges according to Mulliken (the numbers are written without zero digit, a.u.). Total energies (taking into account zero vibrations) of systems **A1**, **A2**, and **A3** equal –7793.3359, –7793.2672, –7793.3489 a.u.respectively, potential barrier to reaction **A1** → **A3** is V 43.1 kcal mol^{-1}.
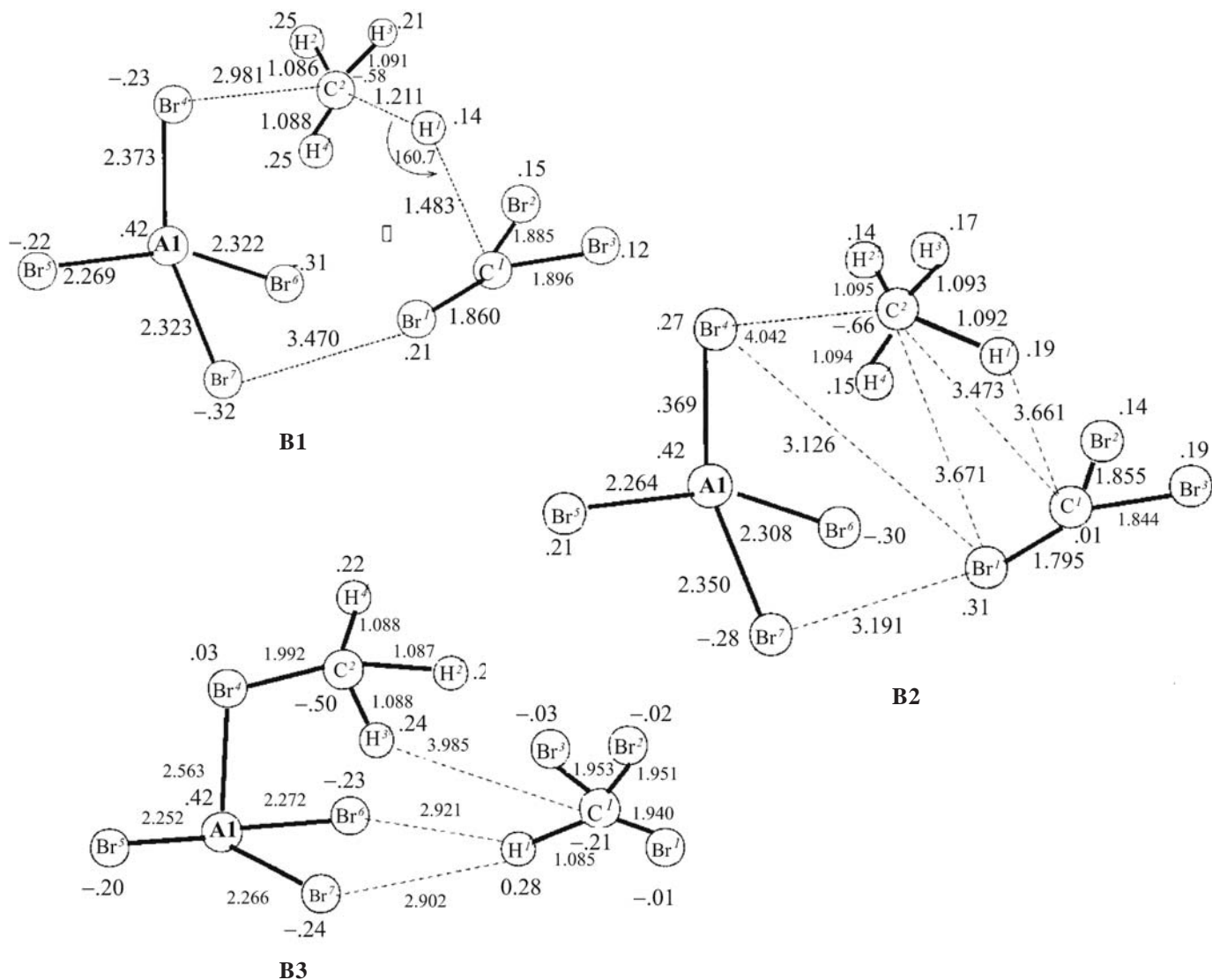
Fig. 2. Methane reaction with complex CBr₃⁺AlBr₄⁻. Structures of initial solvate **B1**, reaction product **B3**, and transition state **B2**. Total energies (taking into account zero vibrations) of systems **B1**, **B2**, and **B3** equal –18323.1441, –18323.1091, –18323.1875 a.u. respectively, potential barrier to reaction **B1** → **B3** is V 22.0 kcal mol⁻¹.

procedures, DFT-B3LYB as well as DFT-PBE, gave results in qualitative agreement with the calculation data obtained by MNDO/PM3 method [24, 25].

Methane reaction with CBr₃⁺AlBr₄⁻ complex (system B). At the approach of methane molecule to cationic complex CBr₃⁺AlBr₄⁻, where the maximum positive charge of the CBr₃⁺ fragment is located on Br^I atom, a number of "solvates" is formed. In Fig. 2 the "solvate" with minimum energy **B1** is represented.

By analysis of calculated by DFT-B3LYP and DFT/PBE methods potential curves describing the energy variation at approach of carbon atoms belonging to electrophile (C^I) and methane (C^2) we established the

positions of maxima and minima. The minima correspond to structure **B3**, bromoform adduct with a donor-acceptor complex of methyl bromide with aluminum bromide. Calculations by B3LYP (programm GAUSSIAN, procedure QST3) and PBE methods of the transition state corresponding to the maximum on PC at transition of initial solvate **B1** to final adduct **B3** gave structures **B2** (Fig. 2). Diagrammatic sketch of these transition states is given in Scheme 5. There in the nearly linear fragment C–H–C hydride transfer occurs from methane to cation moiety CBr₃⁺ of CBr₃⁺AlBr₄⁻ complex. The rupture of hydrogen from methane molecule with its transfer to the C atom of the electrophile is facilitated by the nucleophilic assistance of the unshared electron pair of Br atom of
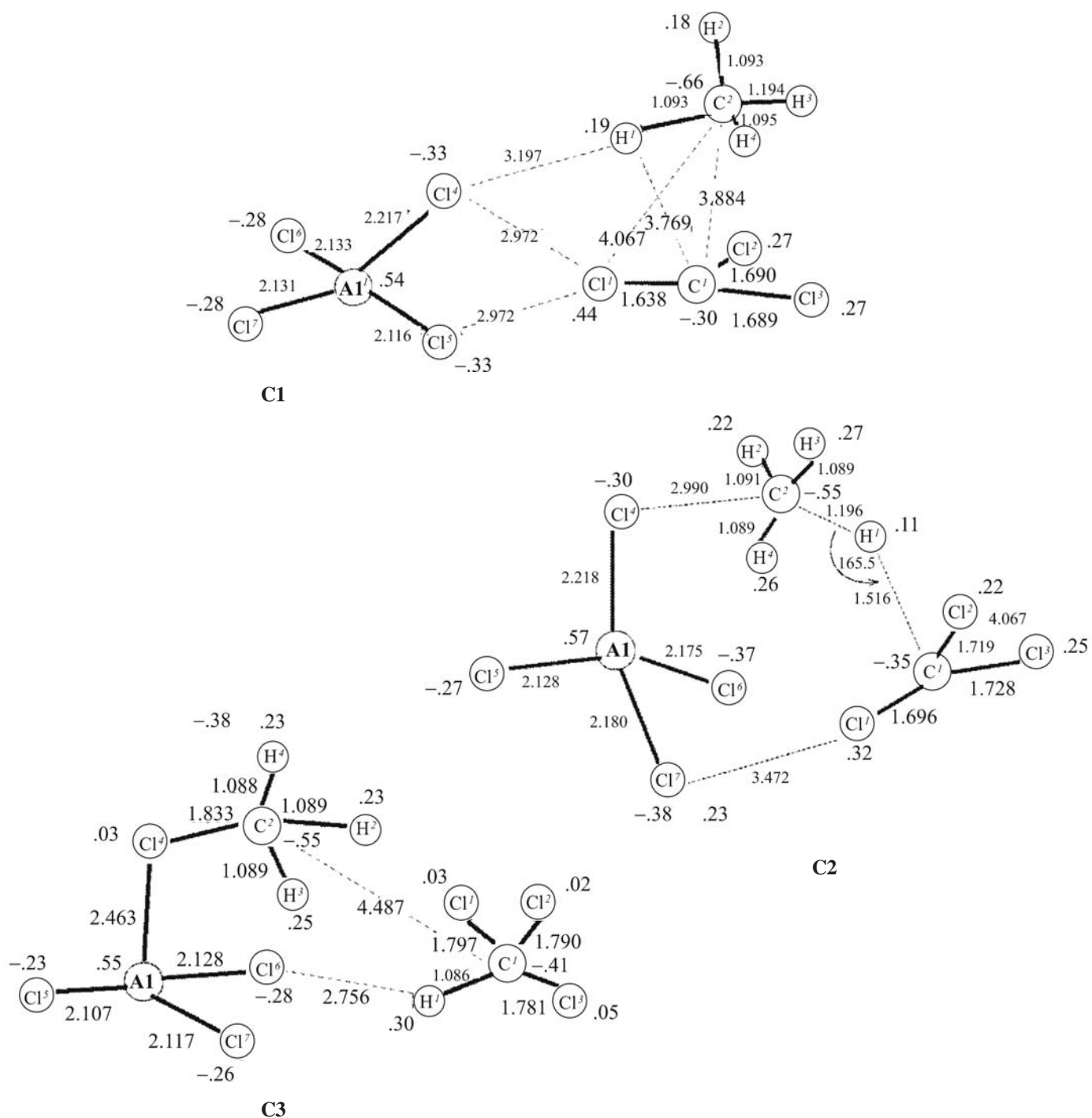
Fig. 3. Methane reaction with complex CCl₃⁺AlCl₄⁻. Structures of initial solvate **C1**, reaction product **C3**, and transition state **C2**. Total energies (taking into account zero vibrations) of systems **C1**, **C2**, and **C3** equal –3542.5219, –3542.4944, –3542.5776 a.u. respectively, potential barrier to reaction **C1** → **C3** is V 17.3 kcal mol⁻¹.

the anion moiety AlBr₄⁻ of CBr₃⁺AlBr₄⁻ complex. This transition state is unprecedented among the known schemes of electrophilic activation of alkanes.

According to PM3 procedure the cyclic transition state found is planar whereas the calculations by means of

B3LYP and PBE methods giving identical results show that the aluminum atom significantly deviates from the plane.

We also carried out additional calculation of structures **B2** and **B3** by HF/6-31G** method. The results obtained
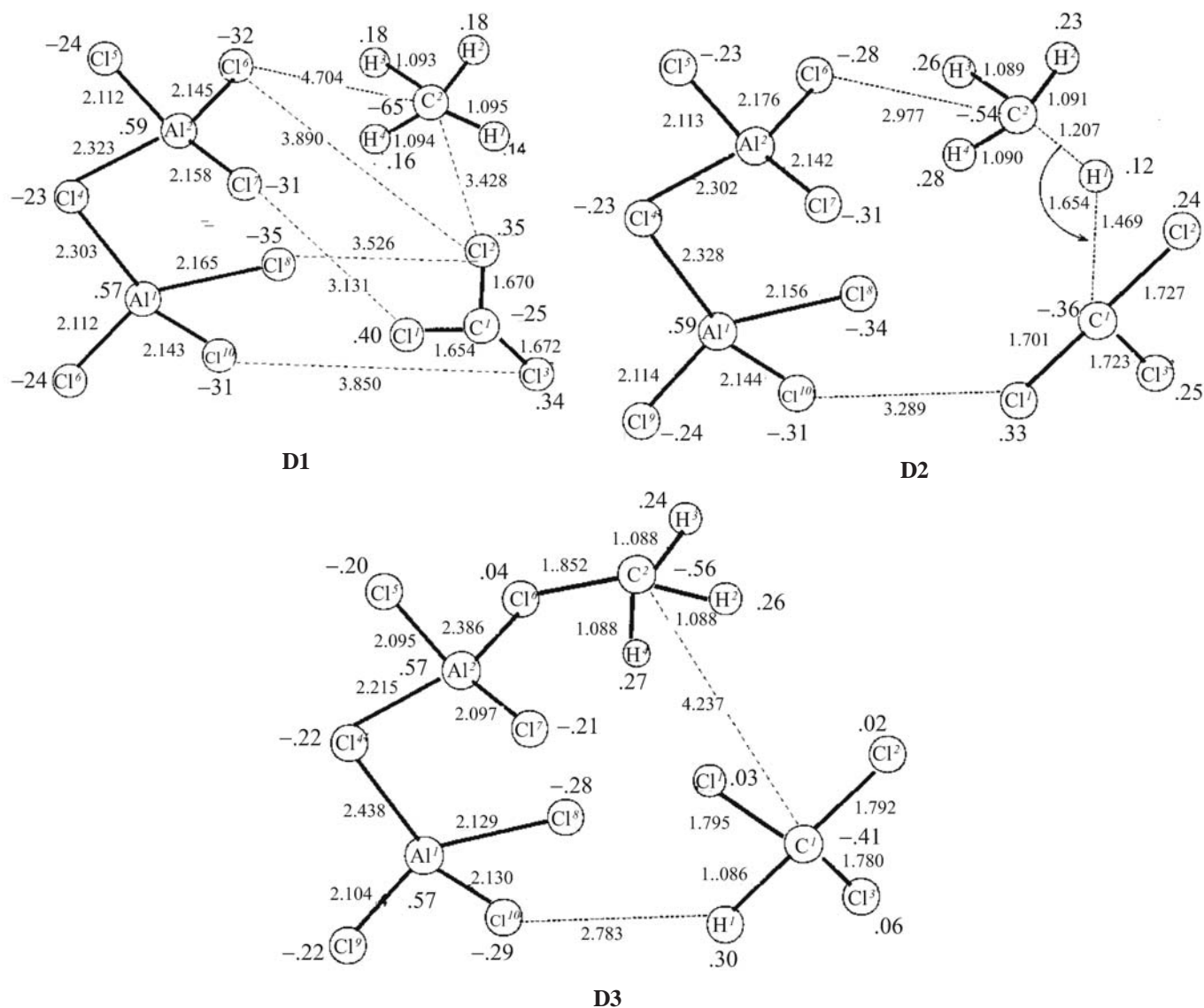
Fig. 4. Methane reaction with complex $CCl_3^+Al_2Cl_7^-$. Structures of initial solvate **D1**, reaction product **D3**, and transition state **D2**. Total energies (taking into account zero vibrations) of systems **D1**, **D2**, and **D3** equal–5165.7872, –5165.7559, –5165.8205 a.u. respectively, potential barrier to reaction **D1** → **D3** is V 19.6 kcal mol^{-1}.

are generally in agreement with the data in Fig. 2: all used methods of calculation show that the structures of transition states correspond to the early stage of hydride transfer from methane to the cation fragment CBr_3^+ of $CBr_3^+AlBr_4^-$ complex. In particular, calculation by HF/6-31G** method gave distance H^1···C^2 1.204 Å, and distance H^1···C^1 1.336 Å.

Methane reaction with electrophile $CCl_3^+AlCl_4^-$ (system C). By means of DFT-B3LYP/6-31G(d) a transformation was studied of one of initial methane solvates of electrophile $CCl_3^+AlCl_4^-$ complex (**C1**) into the final adduct of chloroform and donor-acceptor complex of methyl chloride with aluminum chloride (**C3**). The

transition state **C2** of this transformation (Fig. 3) is totally similar to the transition state **B2** of system **B**. Thus the replacement of chlorine for bromine did not change anything in the course of reaction: the hydride transfer from methane molecule to the C atom of electrophile occurred in the nearly linear fragment C–H–C of the cyclic transition state and was facilitated by the nucleophilic assistance of unshared pair of the Cl atom of the anion moiety going to be transmitted to methane, and the transition state, like in **B** system, corresponded to the early stage of the hydride transfer.

Methane reaction with electrophile $CCl_3^+Al_2Cl_7^-$ (system D). The calculation was carried out by DFT-

B3LYP/6-31G(d) method. In a cyclic transition state **D2** of methane chlorination giving a chloroform adduct with a donor-acceptor complex of methyl chloride and isomer of dimeric aluminum chloride $Cl_2AlClAlCl_3$ (**D3**) the hydride transfer from methane molecule to the C atom of electrophile occurred in the nearly linear fragment C–H–C of the cyclic transition state (Fig. 4) and was facilitated by the nucleophilic assistance of unshared pair of the terminal Cl atom in the anion fragment; just this atom chlorinated the methane molecule. The increased ring in the structure of the transition state due to the larger anion fragment of the electrophile does not change anything in the qualitative characteristic of the transition state, and like those in systems **B** and **C**, it corresponds to the early stage of hydride transfer.

The calculations made in this study by DFT-B3LYP/6-31G(d) and DFT-PBE/3z methods supported the concepts based on MNDO/PM3 calculations of mechanism of methane halogenation by aprotic organic superacids consisting of methane polyhalides and aluminum halides [24, 25]. In cyclic transition states of methane halogenation occurs synchronous hydrogen transfer from C atom of methane to C atom of electrophile within a nearly linear fragment C–H–C of the ring and a generation of the bond between the C atom of methane and the approached to it Hlg atom of electrophile. Potential barriers to halogenation of methane, the most passive among alkanes, are lowered by nucleophilic assistance of the unshared electron pair of the Hlg atom going over to methane. For all the three overall neutral complexes we have considered, for model $CHlg_3^+AlHlg_4^-$ (Hlg = Cl, Br) and, what is more important, for $CCl_3^+Al_2Cl_7^-$ complex which in the real medium does not require dissociation of the aluminum halide dimer, the potential barriers equal approximately 20 kcal mol^{-1}.

The reactions that we have described are well entered into the general context of electrophilic reactions with nucleophilic assistance abundant in the organic chemistry.

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