

# Polyhalomethanes combined with aluminum halides as generators of superelectrophiles of a novel type<sup>1</sup>

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## Abstract

Semi-empirical (AM1) and ab initio (MO LCAO SCF-RHF/6-31G) quantum chemical calculations of  $\text{CCl}_4 \cdot n\text{AlCl}_3$  ( $n = 1, 2$ ) and  $\text{CCl}_3^+\text{AlCl}_3$  systems were performed to elucidate the nature of complexes responsible for the superelectrophilicity of tetrachloromethane in the presence of aluminum chloride. The results of the calculations do not allow us to relate the high activity of these systems with formation of the species  $\text{Cl}_2\text{CCl}^+ \rightarrow \text{AlCl}_3$ . The  $\text{CCl}_4 \cdot n\text{AlCl}_3$  systems were shown to be generators of the superelectrophiles of a novel type, namely the electron deficient 'chloronium' cations  $\text{Cl}_2\text{C}-\text{Cl}^+$  and dications  $\text{Cl}^+-\text{C}-\text{Cl}^+$  which are different from the known chloronium cations  $\text{R}-\text{Cl}^+-\text{R}$ . The capability of forming mono-, di- and tridentate ionic complexes, wherein  $\text{Cl}^+$  of the  $\text{CCl}_3^+$  cation is bonded with one, two or three  $\text{Cl}^-$  of  $\text{AlCl}_4^-$ , is a peculiarity of the  $\text{CCl}_3^+\text{AlCl}_4^-$  system. The bidentate complex  $\text{CCl}_3^+\text{AlCl}_4^-$  with positive charge 0.54 a.u. on the Cl atom (instead of 0.33 a.u. in a free  $\text{CCl}_3^+$ ) seems to be the best candidate for the role of key superelectrophile in the  $\text{CCl}_4 \cdot n\text{AlCl}_3$  systems. © 1997 Elsevier Science S.A.

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## 1. Introduction

The acidic activation of polyhalomethanes has been known since 1950 when exchange of chlorine atoms of  $\text{CCl}_4$  with  $^{36}\text{Cl}$  in labeled  $\text{AlCl}_3$  at  $-20^\circ\text{C}$  was observed [1]. Later,  $\text{CCl}_4$  in combination with  $\text{AlCl}_3$  was found to be a good chlorinating system for adamantane [2]. Olah et al. [3] described chlorination and bromination of alkanes and cycloalkanes by  $\text{CH}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in the presence of  $\text{SbF}_5$  or  $\text{HF}-\text{SbF}_5$ . Sommer and coworkers [4,5] have found that non-effective and non-selective carbonylation of propane in  $\text{HF}-\text{SbF}_5$  becomes effective and selective in the presence of  $\text{CCl}_4$  or  $\text{CHCl}_3$ . Vancik et al. [6] have found that, whereas cyclohexane (or hexanes) did not ionize in  $\text{SbF}_5$  or  $\text{HF}-\text{SbF}_5$ , its ionization occurred rapidly at  $150^\circ\text{K}$  in the presence of  $\text{CCl}_4$  with formation of  $\text{CHCl}_3$  and methylcyclopentyl (or methylpentyl) cation.

Recently, we have found that polyhalomethanes in combination with aluminum halides exhibit the properties of the strongest aprotic organic superacids [7–15].

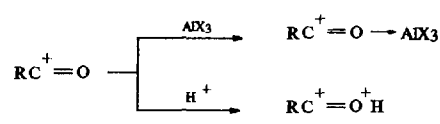
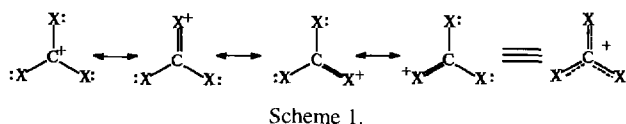
They effectively initiate cracking, oligomerization, isomerization of n-alkanes [7] and selective functionalization reactions, such as ionic monobromination of n-alkanes and cycloalkane, and dibromination of ethane with  $\text{Br}_2$  [8,9], carbonylation of alkanes [10] and cycloalkanes, [11,12], formylation of adamantane [13] with CO, alkylation of passivated aromatics with alkanes [14,15].

The nature of active species generating from halomethanes in the presence of protic and aprotic acids is unknown. Olah et al. [16] have observed by  $^{13}\text{C}$  NMR the formation of trihalomethyl cations from tetrahalomethanes under the action of an excess of  $\text{SbF}_5$  in  $\text{SO}_2\text{ClF}$ . However, on the basis of the concept of the carbocation nature of the trihalomethyl cations with efficient p–n interaction between a positive charged carbon atom and non-bonded electron pairs of halogenes (Scheme 1), Olah concluded that these cations are electrophiles of only moderate strength and so are themselves incapable of abstracting hydride ion from alkanes [17].

Two recent theoretical studies were devoted to elucidation of the nature of superelectrophiles generated from polyhalomethanes under the action of aprotic [18] and protic [19] acids.

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<sup>1</sup> Dedicated to the memory of Professor Yuri Struchkov.



Semi-empirical calculations of the complexes  $\text{CBr}_4 \cdot n\text{AlBr}_3$  ( $n = 1, 2, 4$ ) and free cations  $\text{CX}_3^+$ ,  $\text{CHX}_2^+$ ,  $\text{CHX}^+$ ,  $\text{CX}_2^{2+}$  [18] demonstrated that trihalomethyl cations  $\text{CX}_3^+$  and dihalomethyl dicationic species  $\text{CX}_2^{2+}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) – both free and bound in ionic complexes  $\text{CBr}_3^+ \text{Y}^-$  and  $\text{CBr}_2^{2+} \text{Y}_2^-$  ( $\text{Y} = \text{AlBr}_4^-, \text{Al}_2\text{Br}_7^-$ ) – strictly speaking, are not carbenium cations (or their complexes), since the positive charge in the cationic species is located on monocoordinated halogen atoms while carbon atoms carry negative charges. Therefore these cations and dicationic species can be considered as halogenonium ions, differing from halogenonium salts with dicoordinate halogen atoms.

A remarkable peculiarity of these ionic bromonium complexes is the fact that the positive charged bromine atoms attached to the carbon atom and the negative charged bromine atoms of the  $\text{AlBr}_4^-$  (or  $\text{Al}_2\text{Br}_7^-$ ) anion are involved in the formation of the ionic bonds. The results of this study show that among these complexes there are some highly electrophilic ones which could be responsible for the superacidic reactivity of the  $\text{CBr}_4 \cdot n\text{AlBr}_3$  systems. Formation of these complexes requires more than 25 (cationic) and 90  $\text{kcal mol}^{-1}$  (dicationic), hence the thermodynamic conditions of their formation (at least in the case of the dicationic complexes) are unfavorable [18].

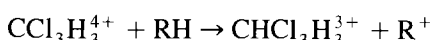
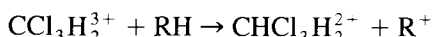
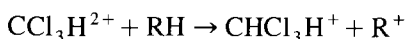
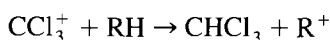
On the other hand, one can believe that protosolvation (or formation of a donor–acceptor bond with Lewis acid) of a halomethyl cation should enhance the electrophilic character of the cationic species (Scheme 2).

The idea of an important role of multicharged species in electrophilic organic reactions is becoming more and more popular [17,20–24]. For instance, all chemical and

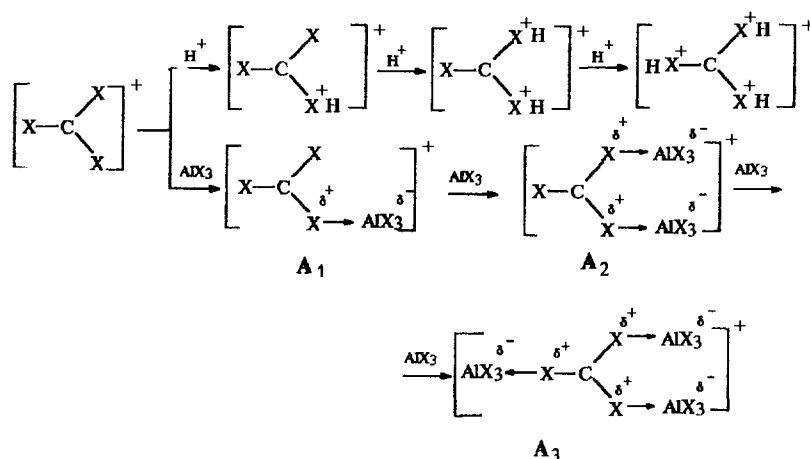
physicochemical data and the results of calculations for complexes  $\text{RCOX} \cdot n\text{AlX}_3$  [22–25] ( $\text{R} = \text{Alk}, \text{Ar}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ;  $n = 1, 2$ ), as well as for acylium salts in proton superacid media [17,21,26], allowed us to assume the key role of species of the dication type in reactions of these systems with alkanes and arenes (Scheme 3).

Protonated halomethyl cations (Scheme 2) were a subject of non-empirical calculations [19]. These species were shown to have considerable kinetic stability. Although the calculated kinetic barriers for monoprotection of halomethyl cations  $\text{CX}_3^+$  amount to 70–84  $\text{kcal mol}^{-1}$ , and for diprotection 156–171  $\text{kcal mol}^{-1}$ , these monoprotected dicationic species  $\text{CX}_3\text{H}^{2+}$  and even diprotected tricationic species  $\text{CX}_3\text{H}_2^{3+}$  are rather stable to deprotonation. This indicates that once formed these multicharged cations should be kinetically stable. For example, calculated protodissociation barriers for  $\text{CBr}_3\text{H}^{2+}$ ,  $\text{CBr}_3\text{H}_2^{3+}$  and  $\text{CBr}_3\text{H}_3^{4+}$  are 74, 37 and 8  $\text{kcal mol}^{-1}$  respectively, indicating the kinetic stability of  $\text{CBr}_3\text{H}^{2+}$  and  $\text{CBr}_3\text{H}_2^{3+}$  cations.

Protonation dramatically increases the activity of the trichloromethyl cation in reactions with alkanes estimated according to the heats of the following isodesmic reactions with propane ( $\text{RH} = \text{C}_3\text{H}_8$ ):



The enthalpies of the above exothermic reactions increase with the number of protonated chlorine atoms,

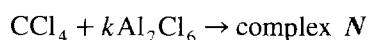
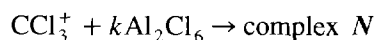


and amount to 3.9, 145.5, 296.4 and 423.8 kcal mol<sup>-1</sup> respectively.

The main subject of the present investigation is the problem of the existence of complexes  $A_1$ – $A_3$  (Scheme 2) analogous to the protonated forms of the trichloromethyl cation. The search for other superelectrophiles that could play a key role in reactions of alkanes with polyhalomethanes in the presence of aluminum halides was also performed. With this goal, the fragments of potential energy surfaces (PES) of systems  $CCl_3^+ \cdot AlCl_3$  and  $CCl_4 \cdot nAlCl_3$  ( $n = 1, 2$ ) were studied by quantum-chemical methods. Calculations were performed in the valence approximation by the semi-empirical AM1 method with full optimization of geometry. In some cases (where it was possible) the ab initio calculations at the MO LCAO SCF-RHF/6-31G level were also carried out. Calculations were performed with the GAMESS program package [27] adapted for the Workstation DEC Alpha AXP 3000-400.

## 2. Results and discussion

The main results of the calculations (bond lengths, effective charges on atoms) for cation  $CCl_3^+$  (1), dication  $CCl_2^{2+}$  (2), monoprotonated (3) and diprotonated (4) trichloromethyl cation and the products of interaction of  $CCl_3^+$  with  $AlCl_3$  (5, 6) and with  $HCl$  (7) are given in Fig. 1. The heats of formation ( $\Delta H_f^\circ$ ) of ions and complexes and enthalpies ( $\Delta_r$ ) of reactions



are given in Table 1.

Ions 1–4 were studied in detail in the work of Ref. [19] by ab initio methods. The results of our present AM1 calculations of these ions coincide qualitatively with those described in Ref. [19]. We would like to pay attention here to a point that was not discussed in Ref.

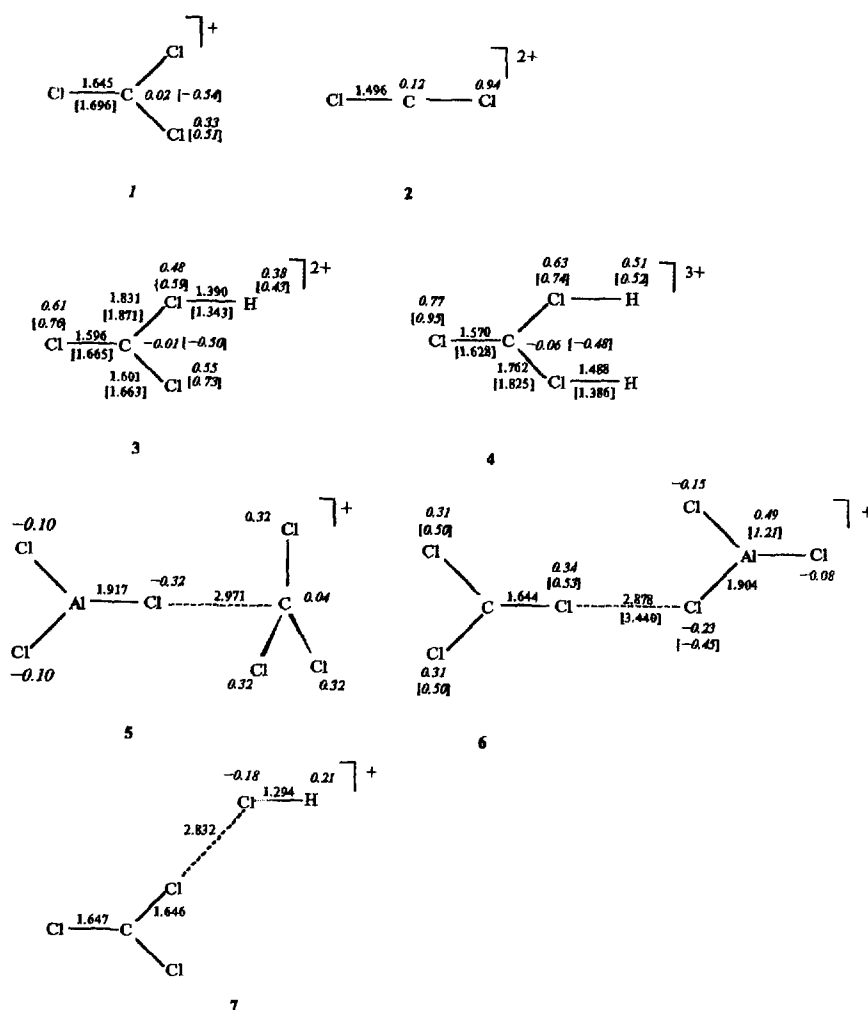


Fig. 1. Some results of calculations (bond lengths, atomic charges (italic)) by the AM1 and ab initio (in brackets) methods for cations 1–7.

Table 1

Heats of formation ( $\Delta H_f$  (kcal mol<sup>-1</sup>)) of molecules, ions, complexes; enthalpies of reactions ( $\Delta_r$  (kcal mol<sup>-1</sup>)) calculated by methods AM1 and ab initio RHF/6-31G<sup>a</sup>; total energies in the ab initio RHF/6-31G calculations ( $E_t$  (a.u.))

Complex	AM1		Ab initio	
	$\Delta H_f$	$\Delta_r$	$E_t$	$\Delta_r$
1	201.6	—	-1415.81632	—
2	612.1	—	—	—
3	554.7	—	-1415.77935	—
4	1018.7	—	-1415.55893	—
5	56.8	-14.7 <sup>b</sup>	-3036.28317	-11.3 <sup>b</sup>
6	57.7	-15.6 <sup>b</sup>	-3036.29133	-6.2 <sup>b</sup>
7	172.5	—	—	—
8	-174.8	-12.8 <sup>c</sup>	—	—
9	-148.4	-39.2 <sup>c</sup>	-3496.05850	-36.7 <sup>c</sup>
10	-134.7	-52.9 <sup>c</sup>	-3496.04469	-41.3 <sup>c</sup>
11	-131.4	-56.2 <sup>c</sup>	-3496.04443	-41.5 <sup>c</sup>
12	-249.3	-97.7 <sup>d</sup>	—	—
13	-271.9	-75.1 <sup>d</sup>	-5061.62560 <sup>e</sup>	—

<sup>a</sup> Heats of formation of the following systems were used (kcal mol<sup>-1</sup>): -28.1 (CCl<sub>4</sub>), -140.3 (AlCl<sub>3</sub>), -250.6 (AlCl<sub>4</sub><sup>-</sup>), -318.9 (Al<sub>2</sub>Cl<sub>6</sub>).

<sup>b</sup> Enthalpy of reaction CCl<sub>3</sub><sup>+</sup> + 1/2 Al<sub>2</sub>Cl<sub>6</sub> → complex N.

<sup>c</sup> Enthalpy of reaction CCl<sub>4</sub> + 1/2 Al<sub>2</sub>Cl<sub>6</sub> → complex N.

<sup>d</sup> Enthalpy of reaction CCl<sub>4</sub> + Al<sub>2</sub>Cl<sub>6</sub> → complex N.

<sup>e</sup> STO-3G calculation.

[19], namely the charge distribution in these ions. In full agreement with the results of Ref. [18], positive charges on CCl<sub>3</sub><sup>+</sup> and CCl<sub>2</sub><sup>2+</sup> ions are mainly located on chlorine atoms. The protonation does not change the character of the electron density distribution in the CCl<sub>3</sub><sup>+</sup> cation, i.e. the positive charges are concentrated as before on the chlorine atoms. Moreover, while the positive charges on Cl atoms upon protonation are noticeably increased, the electron density on the C atom changes insignificantly (it is curious that it rises). In the protonated species the maximal charges are concentrated naturally on the remaining unprotonated chlorine atoms.

In search for the donor–acceptor complex [Cl<sub>2</sub>CCl]<sup>+</sup> → AlCl<sub>3</sub>, several variants (a–d) of the disposition of the CCl<sub>3</sub><sup>+</sup> cation toward AlCl<sub>3</sub> at the ‘initial moment’ were considered (Fig. 2). It was accepted that at the initial moment the structure of the CCl<sub>3</sub><sup>+</sup> cationic fragment is the same as for the free CCl<sub>3</sub><sup>+</sup> and the Cl(1) atom which approaches the Al atom lies on the symmetry axis of the AlCl<sub>3</sub> group. In case a AlCl<sub>3</sub> is planar, hence all angles  $\alpha(n) = \text{Cl}(1)\text{–Al–Cl}(n)$  are equal to 90° ( $n = 4, 5, 6$ ) and the Al–Cl(1)–C fragment is linear (attack angle  $\beta = 180^\circ$ , see Fig. 2). In all other cases (b–d), the valence angles in AlCl<sub>3</sub> are tetrahedral, hence the angles Cl(1)–Al–Cl( $n$ ) are tetrahedral and  $\alpha(n) = 109.5^\circ$ . In case b,  $\beta = 180^\circ$ , that is to say Al–Cl(1)–C is linear; in cases c and d, the angles of attack  $\beta$  were admitted to be equal to 109.5° and 90° respectively.

According to the AM1 calculations, in case a both fragments AlCl<sub>3</sub> and CCl<sub>3</sub><sup>+</sup> remain planar, lie in the orthogonal planes and form a slightly bonded system 5 in which the chlorine atom of the CCl<sub>3</sub><sup>+</sup> is not bonded to aluminum but the chlorine atom of AlCl<sub>3</sub> is coordinated to the carbon atom of CCl<sub>3</sub><sup>+</sup>. In cases b–d, only a monodentate cationic complex 6 is formed, irrespective of the initial arrangement of fragments AlCl<sub>3</sub> and CCl<sub>3</sub><sup>+</sup>. In the complex 6, AlCl<sub>3</sub> does not play its traditional role of an acceptor of an electron pair. On the contrary, in this complex the negative charged Cl of AlCl<sub>3</sub> is electrostatically bonded with the positive charged chlorine atom of the cation. The reactions of formation of 5 and 6 from the fragments are slightly exothermic (4.5 and 3.6 kcal mol<sup>-1</sup>), so that AlCl<sub>3</sub> in these complexes acts as if it solvates the CCl<sub>3</sub><sup>+</sup> cation.

It is interesting that in the course of our study we found a complex 7 which is quite analogous to 6 (see Fig. 1). The formation of 7 can be visualized as the result of the interaction either of the dication CCl<sub>3</sub>H<sup>2+</sup> with the Cl<sup>-</sup> anion or of the CCl<sub>3</sub><sup>+</sup> cation with HCl. Complex 7 is formed even if the species HCl is oriented initially with its proton center towards the CCl<sub>3</sub><sup>+</sup> group. In this complex as well as in complex 6, positive and negative charged chlorine atoms are bonded electrostatically.

The results of investigations of the fragments of PES of the CCl<sub>3</sub><sup>+</sup>AlCl<sub>3</sub> system by the ab initio method at 6-31G basis are in agreement with the above data of the AM1 calculations. Starting from similar initial arrangements (a–d), the geometry optimization results either in the system of two very weakly bonded initial fragments or in an ionic complex analogous to the complex 6.

It should be emphasized that the AM1 method leads to decreased values for all bond lengths and for charges on atoms compared with those calculated by the ab initio method.

Thus, our attempts to find the local minima corresponding to the complex of A<sub>1</sub> type (Scheme 2) on the PES of the CCl<sub>3</sub><sup>+</sup>·AlCl<sub>3</sub> system by both AM1 and ab initio methods were unsuccessful.

Since we failed to find the analogs of protonated trihalomethyl cations in the system CCl<sub>3</sub><sup>+</sup>·AlCl<sub>3</sub> (as well as CCl<sub>3</sub><sup>+</sup>2AlCl<sub>3</sub>), we focused our attention on a detailed study of the systems CCl<sub>4</sub>·nAlCl<sub>3</sub> ( $n = 1, 2$ ).

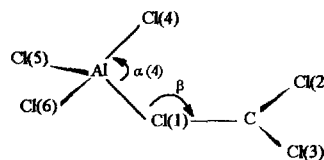


Fig. 2. The initial disposition of fragments, used in the search for donor–acceptor complex CCl<sub>3</sub><sup>+</sup> → AlCl<sub>3</sub>:  $\alpha(n) = \text{Cl}(1)\text{–Al–Cl}(n)$ ,  $n = 4\text{–}6$ ;  $\beta = \text{Al–Cl}(1)\text{–C}$ ;  $\text{Cl}(1)\text{–C–Cl}(n) = 120^\circ$ ,  $n = 2, 3$ ;  $\text{C–Cl}(1) = 1.75 \text{ \AA}$ ;  $\text{C–Cl}(2) = \text{C–Cl}(3) = 1.65 \text{ \AA}$ ;  $\text{Al–Cl}(n) = 1.9 \text{ \AA}$ ,  $n = 4\text{–}6$ ;  $\text{Al–Cl}(1) = 2.3\text{–}2.5 \text{ \AA}$ .

The results of the calculations of the complexes  $\text{CCl}_4 \cdot \text{AlCl}_3$  and some complexes of  $\text{CCl}_4 \cdot 2\text{AlCl}_3$  are summarized in Fig. 3. Four local minima were found on the PES of system  $\text{CCl}_4 \cdot \text{AlCl}_3$ . They correspond to the structures **8–11**. The major minimum corresponds to the donor–acceptor complex **8** with a weak bond  $\text{Cl} \rightarrow \text{AlCl}_3$  and insignificant changes in geometry and charges on atoms compared to the initial  $\text{CCl}_4$  and  $\text{AlCl}_3$  molecules. Three other minima correspond to mono- (**9**), bi- (**10**) and tridentate (**11**) cationic complexes  $\text{CCl}_3^+ \text{AlCl}_4^-$ .

An important feature of these complexes is a significant enhancement of the positive charges on chlorine in bi- (**10**) and tridentate (**11**) complexes, compared with both the free  $\text{CCl}_3^+$  and the  $\text{CCl}_3^+$  bonded monoden-

tately (**9**). The maximal charge 0.53 a.u. is on the Cl atom in the complex **10**. This charge is by 0.2 a.u. higher than in the free  $\text{CCl}_3^+$ .

The ab initio calculations of complexes **9–11** at the 6-31G basis lead to qualitatively similar results. And again, the values for all bond lengths and for all charges, both positive and negative, are larger in the ab initio calculations.

Note also that the ab initio method leads to more favorable energies for formation of the complexes **8–11** and decreases the difference in energies between them.

For systems with composition  $\text{CCl}_4 \cdot 2\text{AlCl}_3$ , two local minima were found on the PES. These minima correspond to complexes **12** and **13**.

Upon calculation of the structure of **12**, we consid-

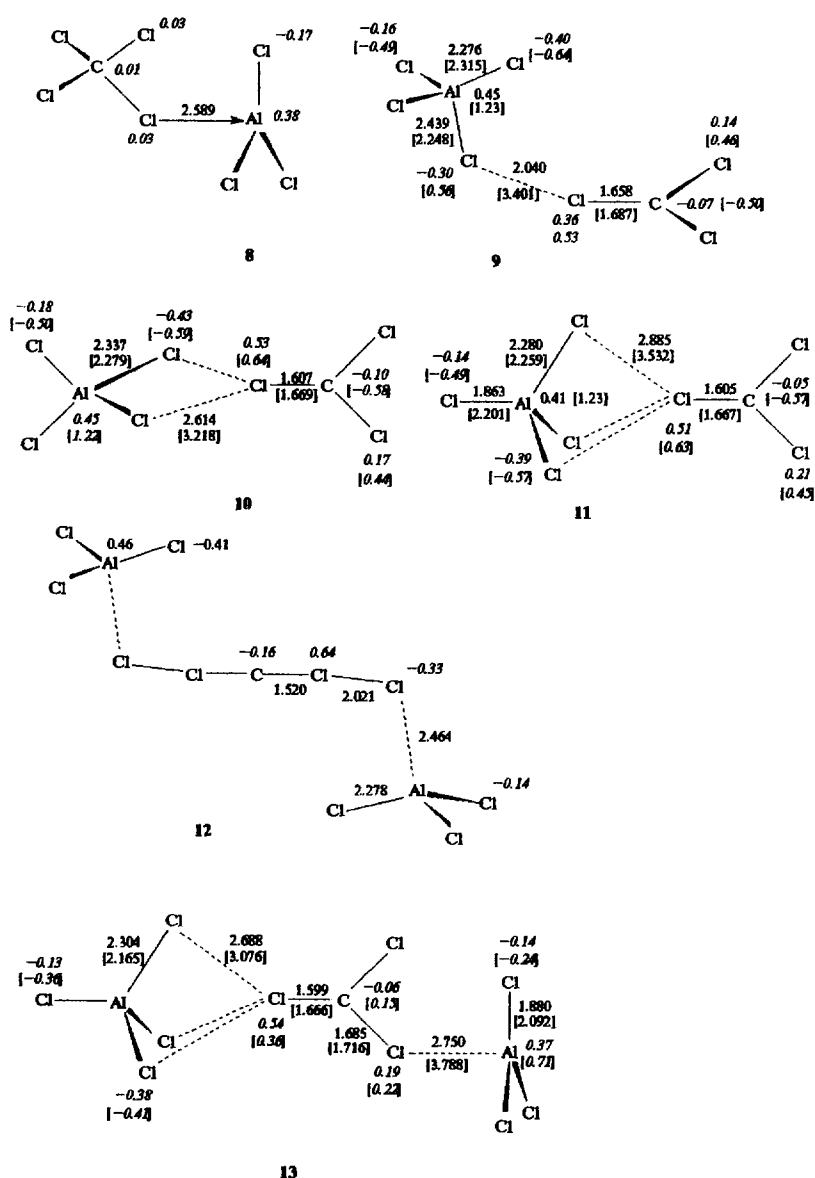


Fig. 3. Some results of calculations (bond lengths, atomic charges (italic)) by the AM1 and ab initio (in brackets) methods for complexes **8–13**.

ered the system consisting of dication **2** and two anions  $\text{AlCl}_4^-$ , bidentately coordinated to Cl atoms of the  $\text{CCl}_2^{2+}$  fragment. However, upon optimization this complex transforms into structure **12**. Complex **12** consists of a linear fragment  $\text{Cl}^- - \text{Cl}^+ - \text{C} - \text{Cl}^+ - \text{Cl}^-$ , whose end atoms are bonded to two molecules of  $\text{AlCl}_3$  via donor–acceptor bonds. The linear fragment of this complex can be considered as an isomer of tetrachloromethane (the local minimum of this isomer lies higher by  $90 \text{ kcal mol}^{-1}$  than the major one corresponding to  $\text{CCl}_4$ ) with strongly polar C–Cl and Cl–Cl bonds.

The positive charges on chlorine of the  $\text{CCl}_2^{2+}$  moiety in the complex **12** turn out to be the highest among all the complexes considered. However, the reaction of the formation of **12** from  $\text{CCl}_4$  and  $\text{Al}_2\text{Cl}_6$  is strongly endothermic.

Complex **13** represents the cationic complex wherein one chlorine atom of  $\text{CCl}_3^+$  is tridentately bonded to  $\text{AlCl}_4^-$  and the other one is bonded to  $\text{AlCl}_3$  via a very weak donor–acceptor bond  $\text{Cl} \rightarrow \text{AlCl}_3$ . This complex can be considered as  $\mathbf{11} \rightarrow \text{AlCl}_3$  and has a structure similar to **A**<sub>1</sub> in Scheme 2. Nevertheless, the maximal charge on chlorine in this complex is only by 0.01 and 0.03 a.u. higher compared to  $\text{Cl}^+$  in cation complexes **10** and **11**.

The reason for such negligible changes in charge in the donor–acceptor complexes is due to the weakness of the donor–acceptor bond considered.

Let us compare the donor–acceptor complexes of  $\text{AlCl}_3$  with the hypothetical linear isomer  $\text{CCl}_4$ , molecule  $\text{CCl}_4$ , complex **11** and  $\text{CCl}_3^+$ . Our calculations show that the decrease in electron density on the Cl atoms of these species ( $-0.45$ ,  $-0.1$ ,  $+0.21$ ,  $+0.33$  a.u.) hinders the formation of the donor–acceptor bond  $\text{Cl} \rightarrow \text{AlCl}_3$  (the strengths of these bonds are  $17.5$ ,  $6.4$ ,  $0.2 \text{ kcal mol}^{-1}$  and no bond respectively). It is seen that for species carrying positive charge the  $\text{Cl} \rightarrow \text{AlCl}_3$  donor–acceptor bonds are very weak and therefore – and this is even more important for our purpose – they cannot lead to any noticeable increase in positive charges compared with corresponding non-coordinated species.

Thus, even if the donor–acceptor complexes of halomethyl cations of the type **A** were formed, their formation would not be accompanied by any enhancement of the electrophilicity of the cations.

Similar results follow from the ab initio calculations. Our attempts to calculate the complex **13** by the ab initio method at the 6-31G basis were unsuccessful. According to the ab initio calculation at the STO-3G basis, a structure qualitatively similar to **13**, depicted in Fig. 3, was found.

The present AM1 calculations for  $\text{CBr}_3^+ \cdot \text{AlBr}_3$  and  $\text{AlBr}_4^- \cdot \text{CBr}_3^+ \rightarrow \text{AlBr}_3$  systems have led to qualitatively close results.

### 3. Conclusion

Thus, these calculations do not allow us to relate superelectrophilic properties of  $\text{CCl}_4 \cdot n\text{AlCl}_3$  systems with the formation of the donor–acceptor complexes of  $\text{CCl}_3^+ \rightarrow n\text{AlCl}_3$  type.

On the basis of the results of the present study and of Ref. [18], we believe that the key role in the reactions of  $\text{CX}_4 \cdot n\text{AlX}_3$  systems with alkanes and arenes belongs to superelectrophiles of a novel type, namely cationic complexes of halogenonium, containing monocoordinated positive charged halogen atoms directly attached to a strongly electron deficient carbon center  $\text{X}_2\text{C}-\text{X}^+$  or  $\text{X}^+-\text{C}-\text{X}^+$ . These halogenonium cations are fundamentally different from known halogenonium ions  $\text{R}-\text{X}^+-\text{R}$ .

The most probable candidate for the role of the key superelectrophile in the  $\text{CCl}_4 \cdot n\text{AlCl}_3$  systems seems to be the bidentate complex **10** with charge on  $\text{Cl}^+$  equal to 0.54 (AM1) or 0.64 a.u. (ab initio) (instead of 0.33 or 0.51 a.u. respectively for free  $\text{CCl}_3^+$ ). The formation of this complex requires about 53 (AM1) or  $33.2 \text{ kcal mol}^{-1}$  (ab initio). It should be stressed that effects of solvation and agglomeration may shift the thermodynamic conditions for cationic complex formation to a more favorable region. The formation of the dicationic complex **12** carrying more charged chlorine (0.64 a.u.) seems to be markedly less favorable, since it requires about  $100 \text{ kcal mol}^{-1}$ . This conclusion is in agreement with the chemical data testifying that the  $\text{CX}_4 \cdot n\text{AlX}_3$  systems exhibit activity both at  $n = 2$  and  $n = 1$  which distinguishes them from the  $\text{RCOX} \cdot n\text{AlX}_3$  complexes displaying activity only at  $n > 1$  [23]. Thus, the formation of active systems from polyhalomethanes does not require an excess of aluminum halide.

The elucidation of mechanisms of alkane and arene activation by halogenonium cations and the pathways by which a hydride ion from alkane (or an aromatic fragment from arene) transfers to the trihalomethyl carbon atom deprived of positive charge needs a further detailed investigation.



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