Electronic structure, geometry, and stability of organic cations, dications, and donor-acceptor complexes

2.* Polyhalomethane complexes with aluminum halides

A. L. Chistyakov, I. V. Stankevich, I. S. Akhrem, N. P. Gambaryan, and M. E. Vol'pin*

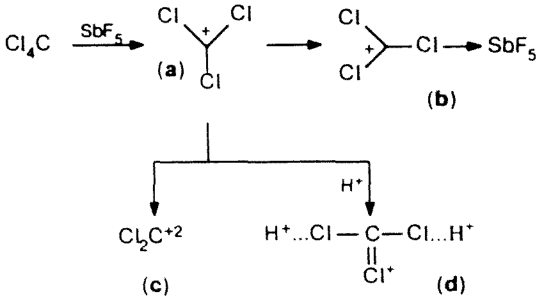
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: stan@ineos.ac.ru

Geometric, electronic, and energy characteristics of the complexes formed in the $CF_4 \cdot nAlF_3$ (n = 1 or 2) and $CBr_4 \cdot nAlBr_3$ (n = 1, 2, or 4) systems have been determined by the semiempirical AM1 method. Besides the donor-acceptor complexes, the $CBr_3^+...AlBr_4^-$, $CBr_3^+...Al_2Br_7^-$, $CBr_2^{2+}...(AlBr_4^-)_2$, and $CBr_2^{2+}...(Al_2Br_7^-)_2$ ionic complexes can be formed in the $CBr_4 \cdot nAlBr_3$ systems. In the cations and dications of polyhalomethanes (when Hal = Cl, Br, or I) in both the free and bound (included in ionic complexes) states, carbon atoms carry negative charges, the C—Hal bonds are substantially shortened, and the positive charges are located on one-coordinate halogen atoms. These cations and dications can be considered as halenium ions that differ from halonium salts with dicoordinate halogen atoms. In the cationic and dicationic complexes of the $CBr_4 \cdot nAlBr_3$ systems, the maximum positive charges on the Br atoms are 0.39 and 0.94, respectively. Fluorine-containing cations and dications have structures similar to those of carbenium ions, whereas in the $CF_4 \cdot nAlF_3$ systems (n = 1 or 2), only donor-acceptor complexes are formed.

Key words: polyhalomethanes, complexes with aluminum halides, organic cations and dications, donor-acceptor complexes, superelectrophiles, cations and dications of bromenium, quantum-chemical calculations, AM1 method.

Recently, we found that polyhalomethanes exhibit properties of aprotic organic superacids in the presence of $AlBr_3$. Thus, the $CBr_4 \cdot nAlBr_3$, $CHBr_3 \cdot nAlBr_3$ (n = 1 or 2), $CCl_4 \cdot 2AlBr_3$, and $CHCl_3 \cdot 2AlBr_3$ systems effectively catalyze cracking, isomerization, oligomerization, bromination of alkanes and cycloalkanes,[2,3] and carbonylation of cycloalkanes[4,5] under mild conditions. Previously, examples of halogenation,[6] carbonylation,[7] and ionization of saturated hydrocarbons[8] under the action of polyhalomethanes in the presence of SbF_5 and $HF \cdot SbF_5$ have been reported. The nature of the particles responsible for the activity of the $CX_4 \cdot nAlX_3$ systems (X = Hal) is not understood. The structures of trihalomethyl carbenium ion (**a**),[7] trihalomethyl carbocation with the $Cl \rightarrow SbF_5$ coordination bond (**b**),[8] dication (**c**),[9] and ion (**d**)[10] were assigned to the active intermediates formed from polyhalomethanes under the action of SbF_5 and $HF \cdot SbF_5$ (Scheme 1):

Scheme 1



In this work we carried out a quantum-chemical analysis of the species that can be formed in the $CX_4 \cdot nAlX_3$ systems (n = 1—4). Particular attention has been given to the search for structures with high electrophilic properties. These species can be considered as complexes of CX_3^+ cations or CX_2^{2+} dications containing atoms with increased positive charges. In the light of our data and literature data,[10] these species are the most probable candidates for those playing the key role in reactions of alkanes with superelectrophilic systems.

Calculations were performed in the valence approximation by the semiempirical AM1 method[13] with optimization of geometry.

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* For Part 1 see Ref. 1

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 554—560, March, 1996.

Table 1. Heats of formation (ΔH_f^0/kcal mol^{-1}), charges on atoms (q/au), chemical bond lengths (r/ Å), and Wiberg indices (W) calculated by the AM1 methods for CH_kX_{4-k} polyhalomethanes, $[CH_kX_{3-k}]^+$ cations, and $[CH_kX_{2-k}]^{2+}$ dications (k = 0 or 1)

System	ΔH_f^0	q_X	q_C	q_H	r(C—X)	W(C—X)
CF_4	−255.7	−0.14	0.58	—	1.358	0.951
CCl_4	−28.1	−0.01	0.03	—	1.760	0.971
CBr_4	15.9	0.10	−0.40	—	1.918	0.976
CI_4	54.2	0.21	−0.85	—	2.038	0.949
HCF_3	−172.5	−0.17	0.37	0.15	1.368	0.957
$HCCl_3$	−29.0	−0.04	−0.04	0.16	1.748	0.981
$HCBr_3$	6.4	0.07	−0.37	0.17	1.907	0.985
H_2CBr_2	−1.0	0.02	−0.32	0.14	1.902	0.993
H_3CBr	−6.2	−0.04	−0.29	0.11	1.905	0.996
HCI_3	37.8	0.17	−0.68	0.17	2.038	0.964
$[CF_3]^+$	82.1	0.09	0.71	—	1.293	1.236
$[CCl_3]^+$	201.6	0.32	0.02	—	1.645	1.256
$[CBr_3]^+$	243.4	0.43	−0.28	—	1.808	1.254
$[CI_3]^+$	283.2	0.51	−0.52	—	1.960	1.321
$[HCF_2]^+$	121.9	0.07	0.54	0.31	1.290	1.324
$[HCCl_2]^+$	209.1	0.35	0.04	0.25	1.613	1.384
$[HCBr_2]^+$	241.2	0.46	−0.17	0.25	1.771	1.386
$[HCI_2]^+$	272.0	0.53	−0.29	0.23	1.943	1.316
$[FCF]^{2+}$	623.9	0.47	1.06	—	1.207	1.731
$[ClCCl]^{2+}$	612.1	0.94	0.12	—	1.496	1.843
$[BrCBr]^{2+}$	640.6	1.04	−0.07	—	1.647	1.852
$[ICI]^{2+}$	679.6	1.04	−0.08	—	1.839	1.747
$[HCF]^{2+}$	647.3	0.43	1.01	0.56	1.178	2.04
$[HCCl]^{2+}$	661.8	1.05	0.50	0.45	1.470	2.351
$[HCBr]^{2+}$	684.1	1.14	0.44	0.42	1.635	2.336
$[HCI]^{2+}$	706.5	1.12	0.49	0.39	1.848	2.092

Results and Discussion

1. Polyhalomethanes, their cations and dications. Previously, the structural and energy characteristics of polyhalomethanes and their cations were estimated by semiempirical[14,15] and *ab initio*[16–18] methods. However, the values of the effective charges on atoms, which are essential for our purposes, were unavailable in these works. Therefore, we performed independent AM1 calculations of these systems. The geometric and energy parameters we obtained are close to those reported in the literature. The results of our calculations of polyhalomethanes and of the corresponding cations and dications are given in Table 1 and in Fig. 1 (for X = Br).

It is seen from Table 1 that the charge distributions in halomethanes and in the corresponding cations and dications are qualitatively different for X = F, on the one hand, and for X = Cl, Br, and I, on the other. This is in full agreement with the sharp difference in the electronegativities (Pauling[19]) of fluorine (E_F = 4.0) and other halides (E_{Cl} = 3.0, E_{Br} = 2.8, and E_I = 2.5). Only in the case of the fluorine-containing systems are the largest positive charges located on carbon atoms. Therefore, only the $[CF_3]^+$ and $[HCF_2]^+$ cations and the $[CF_2]^{2+}$ and $[HCF]^{2+}$ dications are undoubtedly carbenium ions.

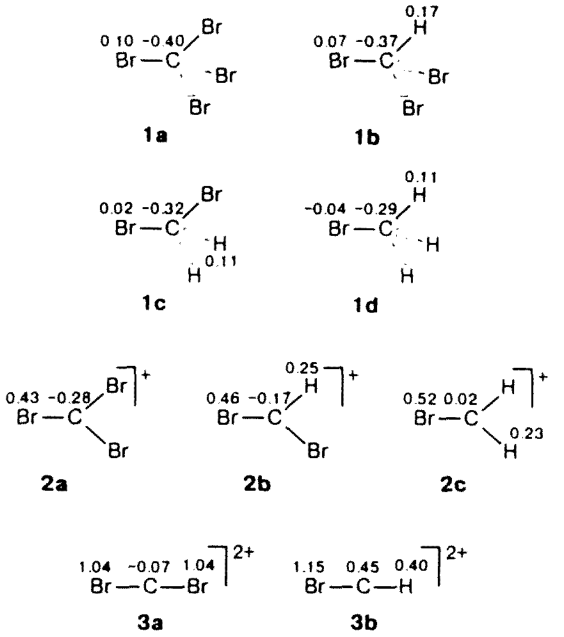


Fig. 1. Effective charges in polybromomethanes and the corresponding cations and dications (see Table 1).

The electron density distributions in the molecules of chloro-, bromo-, and iodomethane as well as in the corresponding anions are similar. Let us consider these distributions using the bromine-containing systems as an example. The structures and the effective charges on atoms in CH_kBr_{4-k} bromomethanes (**1a—d**), $[CH_kBr_{3-k}]^+$ cations (**2a—c**), and $[CH_kBr_{2-k}]^{2+}$ dications (**3a,b**) are shown in Fig. 1. Successive replacement of hydrogen atoms with bromine atoms in methane is accompanied not only by a decrease in the electron density on hydrogen and bromine atoms, which corresponds to the electronegativities of these atoms, but also by an increase in the negative charges on carbon atom, which is inconsistent with the relative electronegativities; this results from the transfer of the lone π electron pairs on bromine atoms to the carbon atom and from the formation of weak π bonds.[20]

Electron density transfer from the bromine to the carbon atom is even more pronounced in cations **2a—c**. This is in agreement with the conclusion[21] that resonance structures with the positive charge on the X atom (Fig. 2) play a substantial role in the CX_3^+ cation (Scheme 2).

Scheme 2

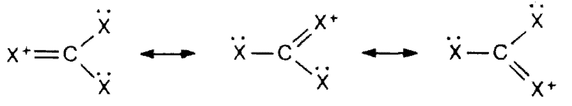


Table 2. Results of calculations by the AM1 method of the $AlBr_3$ (**4**) and Al_2Br_6 (**5a,b**) molecules and $AlBr_4^-$ (**6**) and $Al_2Br_7^-$ (**7**) anions (ΔH_f^0/kcal mol^{-1})

Molecule	Symmetry	ΔH_f^0	Bond	d/Å	W	Angle	φ/deg
4	D_{3h}	−89.4	Al—Br	2.108	1.101	Br—Al—Br	120
5a	D_{2h}	−197.3	Al(1)—Br(1)	2.123	1.078	Al(1)—Br(2)—Al(2)	92
			Al(2)—Br(2)	2.315	0.625	Br(2)—Al(1)—Br(4)	88
						Br(2)—Al(1)—Br(1)	111
						Br(1)—Al(1)—Br(3)	120
5b	C_1	−183.5	Al(1)—Br(1)	2.099	1.210	Al(1)—Br(2)—Al(2)	126
			Al(1)—Br(2)	2.152	0.938	Br(1)—Al(1)—Br(2)	119
			Al(2)—Br(2)	2.549	0.267	Br(2)—Al(2)—Br(3)	93
			Al(2)—Br(3)	2.121	1.090	Br(2)—Al(2)—Br(4)	101
6	T_d	−197.2	Al—Br	2.184	0.977	Br—Al—Br	109
7	C_{2v}	−314.2	Al(1)—Br(1)	2.165	0.946	Al(1)—Br(2)—Al(2)	125
			Al(1)—Br(2)	2.294	0.608	Br(1)—Al(1)—Br(2)	100
			Al(1)—Br(3)	2.156	0.969	Br(2)—Al(1)—Br(3)	108

The electron density transfer to the carbon atom is so large that the positive charge even on the $CBrH_2^+$ cation with only one bromine atom is higher than that on the carbon atom, whereas in the cations with two or three bromine atoms, the carbon atom carries even the negative charge. Therefore, in the strict sense, cations **2a—c** are not the carbenium ions in the classical meaning and may be considered as halenium ions different from the well-studied halonium salts with dicoordinate halogen atoms.[22]

The $[CBr_2]^{2+}$ as well as $[HCBr]^{2+}$ dications **3a,b** (see Fig. 1) isolobal to carbon dioxide correspond to this bromenium type still better. In dication **3a**, the positive charge is located on bromine atoms, whereas the carbon atom carries a small negative charge. In dication **3a**, the C—Br bonds are substantially shorter than those in the CBr_4 and CBr_3^+ cations; their bond orders (Wiberg indices[23]) are substantially higher.

2. The AlX_3 and Al_2X_6 molecules and the AlX_4^- and $Al_2X_7^-$ anions (X = Br or F). The results of calculations by the MNDO and AM1 methods of the heats of formation and the structural characteristics of these systems are partially known.[15,24] The results of our calculations are given in Fig. 2 and in Table 2. Note that the local minimum that corresponds to the unsymmetrical $Br_2AlBr{\rightarrow}AlBr_3$ complex (**5b**) was found on the potential energy surface of the Al_2Br_6 dimer along with the global minimum corresponding to the stable symmetrical Al_2Br_6 structure (**5a**) with two bridge bonds, which have substantial Wiberg indices (0.625; the dimerization energy of $AlBr_3$ is 18.5 kcal mol^{-1}). In complex **5b**, the $Br{\rightarrow}AlBr_3$ coordination bond is longer than the ordinary Br—Al chemical bond and has a small Wiberg index (0.267).

It is believed that according to the proposal of Olah,[9] it is this unsymmetrical dimer with a more electrophilic coordinatively unsaturated Al(1) atom (in **5b**, q(Al(1)) = +0.49, and in **5a**, q(Al(1)) = +0.37) that is responsible for the high activity of aluminum bromide. It is essential that unsymmetrical structure **5b** is only 13.8 kcal mol^{-1} less favorable than symmetrical structure **5a**. Our calculations, which did not take into account the effect of the solvent, did not confirm the proposal of Olah[9] that the Al_2Br_6 dimer occurs in the $AlBr_2^+$...$AlBr_4^-$ ionic form.

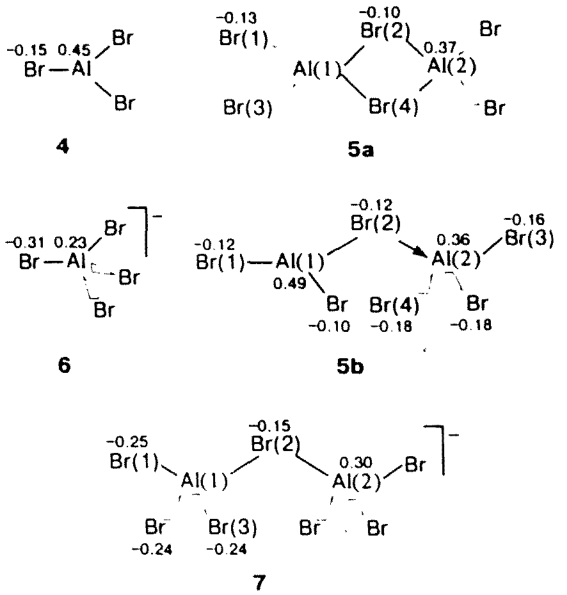


Fig. 2. Molecules $AlBr_3$ (**4**) and Al_2Br_6 (**5a**, **5b**) and anions $AlBr_4^-$ (**6**) and $Al_2Br_7^-$ (**7**) (Table 2).

For AlF_3 and Al_2F_6, the distributions of effective charges on atoms do not differ fundamentally from those typical of the $AlBr_3$ and Al_2Br_6 molecules. As with X = Br, in the case of the Al_2F_6 dimer, the local minimum was found on the potental energy surface; this minimum corresponds to the unsymmetrical $F_2AlF{\rightarrow}AlF_3$ donor-acceptor complex with the value of ΔH_f^0 higher than the heat of formation of the symmetrical form by

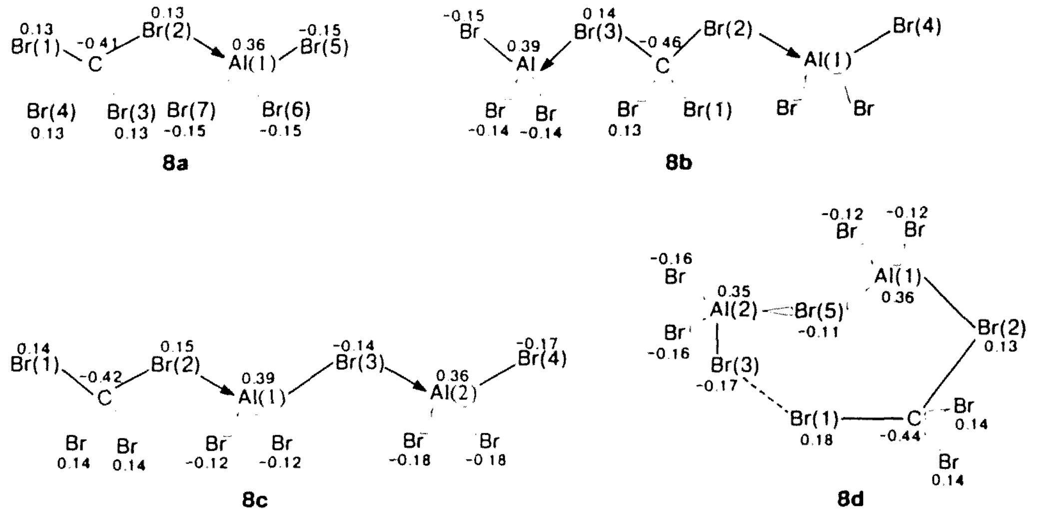


Fig. 3. Donor-acceptor complexes (Table 4).

20.0 kcal mol^{-1}. Note only that the Al—F—Al angle in the unsymmetrical dimer (180°) substantially differs from the corresponding Al—Br—Al angle (126°).

3. Complexes of polyhalomethanes with aluminum halides. We believe that the properties of the $CX_4 \cdot nAlX_3$ systems when X = Cl, Br, or I are qualitatively similar. Therefore, when modeling the molecular and electronic structures of the complexes, which can be generated under the action of aluminum halides on halomethanes, we restricted ourselves to the analysis of the potential energy surfaces of only the $CF_4 \cdot nAlF_3$ (n = 1 or 2) and $CBr_4 \cdot nAlBr_3$ (n = 1, 2, or 4) systems. The results of calculations are given in Table 3 and in Figs. 3—6. For all the structures found, the heats of formation ΔH_f^0 and the heats Δ_i of three decomposition reactions (i = 1—3) that characterize the stability of this $CX_4 \cdot nAlX_3$ complex to the initial reagents are given.

$$CX_4 \cdot nAlX_3 \longrightarrow \begin{cases} CX_4 + nAlX_3 + \Delta_1 & (1) \\ CX_4 + n/_2Al_2X_6 + \Delta_2 & (2) \\ CX_4 + n/_2X_2AlXAlX_3 + \Delta_2 & (3) \end{cases}$$

Table 3. Heats of formation of the complexes in the $CBr_4 \cdot nAlBr_3$ systems and heats of reactions (1)—(3) (kcal mol^{-1}) calculated by the AM1 method

Complex	ΔH_f^0	Δ_1	Δ_2	Δ_3
8a	−75.1	−1.6	7.7	—
8b	−169.1	−6.2	12.3	—
8c	−170.6	−7.7	10.8	−3.0
8d	−176.9	−14.0	4.5	−9.3
9a	−49.4	24.1	33.4	—
9b	−156.2	6.7	25.2	11.4
10a	−86.4	80.4	98.9	—
10b	−288.3	57.3	94.3	—

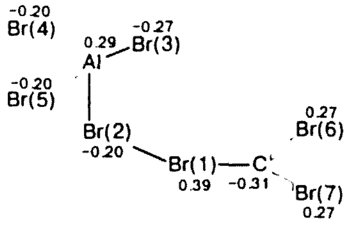
Table 4. Geometric characteristics of the donor-aceptor complexes (AM1)

Complex	Bond	d/Å	W	Angle	φ/deg
8a	C—Br(1)	1.915	0.976	C—Br(2)—Al	118
	C—Br(2)	1.941	0.951	Br(1)—C—Br(2)	108
	Br(2)—Al	2.723	0.178	Br(2)—Al—Br(5)	103
	Al—Br(5)	2.117	1.150	Br(2)—Al—Br(7)	91
8b*	C—Br(2)	1.934	0.926	Br(3)—C—Br(2)	108
	Br(2)—Al(1)	2.826	0.132	C—Br(2)—Al(1)	125
	C—Br(1)	1.912	0.987	Br(2)—Al(1)—Br(4)	74
	Br(4)—Al(1)	1.936	0.960		
8c	C—Br(1)	1.913	0.985	Br(2)—Al(1)—Br(3)	82
	C—Br(2)	1.952	0.933	C—Br(2)—Al(1)	117
	Br(2)—Al(1)	2.626	0.254	Al(1)—Br(3)—Al(2)	125
	Al(1)—Br(3)	2.187	0.854	Br(3)—Al(2)—Br(4)	91
	Br(3)—Al(2)	6.529	0.272		
8d	C—Br(1)	1.926	0.853	Br(1)—C—Br(2)	109
	C—Br(2)	1.972	0.915	C—Br(1)—Br(3)	172
	Br(1)—Br(3)	2.786	0.124	Br(1)—Br(3)—Al(2)	105
	Br(3)—Al(2)	2.174	0.919	Br(3)—Al(2)—Br(5)	102
	Br(2)—Al(1)	2.488	0.374	Al(2)—Br(5)—Al(1)	129
	Al(2)—Br(5)	2.422	0.406	Br(5)—Al(1)—Br(2)	104
	Al(1)—Br(5)	2.207	0.821	Al(1)—Br(2)—C	109

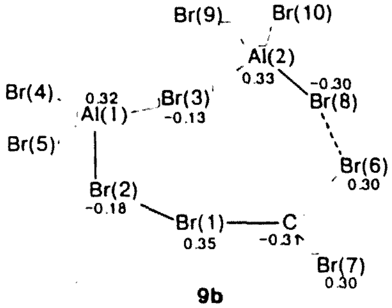
* C_{2v} symmetry.

3.1. Complexes of the $CBr_4 \cdot AlBr_3$ systems. Two local minima were found on the potential energy surface of the system with this composition. The major minimum corresponds to donor-acceptor complex **8a** ($Br_3CBr \rightarrow AlBr_3$, ΔH_f^0 = −75.1 kcal mol^{-1}). The small heat of decomposition reaction (1) when n = 1 (−1.6 kcal mol^{-1}), the insignificantly changes in the geometry and charges on atoms compared to the initial CBr_4 and $AlBr_3$ fragments, the large length of the Br→Al donor-acceptor bond with a low value of the Wiberg index (2.723 Å, 0.178 au), and the absence of the corresponding local minimum when calculations were performed by the MNDO method indicate that this complex is unlikely to play a substantial role in reactions of the $CBr_4 \cdot nAlBr_3$ systems with alkanes.

The second minimum on the potential energy surface is located substantially higher (by ~25.6 kcal mol^{-1}) and corresponds to complex **9a**, which can be described as ionic: $[Br_2CBr]^+[BrAlBr_3]^-$. Of all configurations considered for this complex, the configuration with the $Br^{\delta+}\cdots Br^{\delta'-}$ ionic bond between the positively charged bromine atom of the nearly planar CBr_3^+ cation and the negatively charged bromine atom of the slightly distorted tetrahedral $AlBr_4^-$ anion appeared to be favorable. In this complex, the charges on the carbon and aluminum atoms are even smaller than those in donor-acceptor complex **8a**, but the positive charges on the bromine atoms bonded to the carbon atom and negative charges on the bromine atoms bonded to the aluminum atom (see Figs. 1—4) noticeably increase. It can be proposed that this increase in the polarity should favor stabilization of complex **9a** *via* solvation.



9a



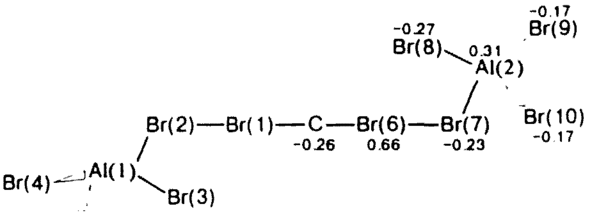
9b

Fig. 4. Complexes containing the CBr_3^+ cationic fragment (Table 5).

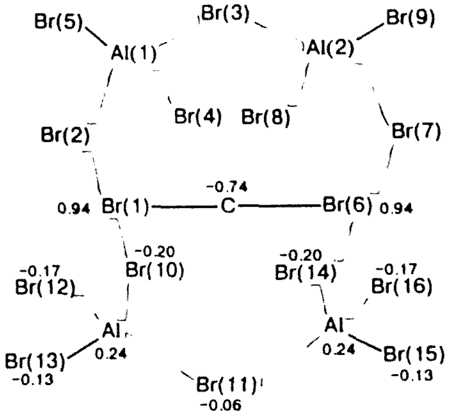
Table 5. Geometric characteristics of the cationic complexes (AM1)

Complex	Bond	d/Å	W	Angle	$\frac{\varphi}{\text{deg}}$
9a	Al—Br(2)	2.330	0.558	Al—Br(2)—Br(1)	104
	Br(1)—Br(2)	2.331	0.446	Br(2)—Br(1)—C	170
	Br(1)—C	1.856	1.894	Br(1)—Br(2)—Al	104
	C—Br(6)	1.808	1.202	Br(2)—Al—Br(3)	100
9b	C—Br(1)	1.871	0.856	C—Br(1)—Br(2)	173
	C—Br(6)	1.805	1.227	Br(1)—Br(2)—Al(1)	107
	Br(1)—Br(2)	2.369	0.384	Br(2)—Al(1)—Br(3)	101
	Br(2)—Al(1)	2.756	0.667	Al(1)—Br(3)—Al(2)	124
	Al(1)—Br(3)	2.252	0.703	Br(3)—Al(2)—Br(8)	105
	Br(3)—Al(2)	2.346	0.509	Br(1)—C—Br(6)	119
	Al(2)—Br(8)	2.170	0.981	Br(1)—C—Br(7)	119

3.2. Complexes of the $CBr_4 \cdot 2AlBr_3$ system. For systems with this composition, five local minima were found on the potential energy surface. Three different donor-acceptor complexes correspond to three local minima with the lowest energies; these minima have close values of the energies. In symmetrical structure **8b**, two bromine atoms of the CBr_4 fragment form donor-acceptor bonds with the aluminum atoms of two $AlBr_3$ molecules (ΔH_f^0 = −169.1 kcal mol^{-1}). In complex **8c**,



10a



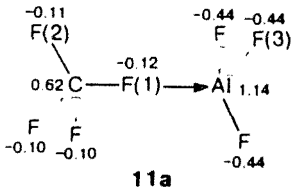
10b

Fig. 5. Complexes containing the CBr_2^{2+} dicationic fragment (Table 6).

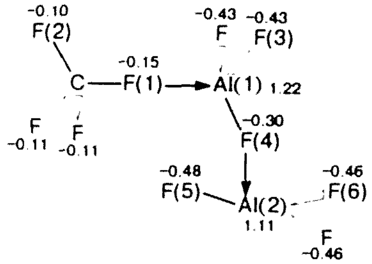
Table 6. Geometric characteristics of the dicationic complexes (AM1)

Complex	Bond	d/Å	W	Angle	$\frac{\varphi}{\text{deg}}$
10a*	C—Br(1)	1.686	1.319	Br(1)—C—Br(6)	180
	Br(1)—Br(2)	2.319	0.455	C—Br(1)—Br(2)	180
	Al(1)—Br(2)	2.372	0.484	Br(1)—Br(2)—Al(1)	104
	Al(1)—Br(3)	2.175	0.980	Br(2)—Al(1)—Br(3)	96
10b**	C—Br(1)	1.618	1.559	Br(1)—C—Br(6)	180
	Br(1)—Br(2)	2.733	0.150	Al(1)—Br(3)—Al(2)	132
	Al(1)—Br(2)	2.223	0.797	Br(3)—Al(2)—Br(8)	107
	Al(1)—Br(4)	2.154	0.982	Br(3)—Al(2)—Br(9)	104
	Al(1)—Br(5)	2.129	1.063		
	Al(1)—Br(3)	2.282	0.635		

* C_2 symmetry. ** D_2 symmetry.



11a



11b

Fig. 6. Complexes of CF_4 with AlF_3 and Al_2F_6 (Table 7).

Table 7. Geometric characteristics of the $CF_4 \cdot AlF_3$ and $CF_4 \cdot Al_2F_6$ donor-acceptor complexes (AM1)

Mole-cule	Bond	d/Å	W	Angle	φ/deg
11a*	C—F(1)	1.381	0.808	C—F(1)—Al	175
	C—F(2)	1.352	0.984	F(1)—C—F(2)	108
	Al—F(1)	1.854	0.276	F(1)—Al—F(3)	96
	Al—F(3)	1.630	0.842		
11b*	C—F(1)	1.391	0.765	C—F(1)—Al(1)	179
	C—F(2)	1.350	0.989	F(1)—C—F(2)	107
	Al(1)—F(1)	1.826	0.315	F(1)—Al(1)—F(3)	98
	Al—F(3)	1.622	0.870	F(1)—Al(1)—F(4)	96
	Al(1)—F(4)	1.678	0.638	Al(1)—F(4)—Al(2)	174
	Al(2)—F(4)	1.761	0.435	F(4)—Al(2)—F(5)	96
	Al(2)—F(5)	1.648	0.784	F(4)—Al(2)—F(6)	103
	Al(2)—F(6)	1.639	0.816		

* C_{2v} symmetry.

the donor-acceptor bond occurs between the bromine atom of the CBr_4 group and the aluminum atom of the unsymmetrical $Br_2AlBrAlBr_3$ dimer, in which the unsymmetrical Al—Br—Al bridge bonds is retained. This complex is slightly stable ($\Delta H_f^0 = -170.6$ kcal mol^{-1}) than isomer **8b**. Finally, complex **8d** has a cyclic configuration with an additional ionic bond between the bromine atoms bonded to the carbon and aluminum atoms (Fig. 3). This complex is energetically most favorable ($\Delta H_f^0 = -176.9$ kcal mol^{-1}).

Complex **9b** (Fig. 4) is substantially less stable, this complex may be conceived as an ionic adduct of the CBr_3^+ cation and the $Al_2Br_7^-$ anion with the $Br^{\delta+}...Br^{\delta'-}$ ionic bond. As in the case of structure **9a**, the charge separation in this complex occurs mainly on bromine atoms bonded to the carbon and aluminum atoms.

The energy of complex **10a** (Fig. 5), which is an ionic adduct of the $[CBr_2]^{2+}$ dication isolobal to carbon dioxide and two $AlBr_4^-$ anions, is even higher (by 90.5 kcal mol^{-1}). The dication is linked to the anions *via* two $Br^{\delta+}...Br^{\delta'-}$ ionic bonds. Positive charges on the bromine atoms of the CBr_2 fragment are 0.66. These bromine atoms may be considered as bromenium centers, *i.e.*, one-coordinate bromine cations. This is consistent with the linear structure of the $Br^{\delta'-}...Br^{\delta+}—C—Br^{\delta+}...Br^{\delta'-}$ fragment ($\angle$CBr(1)Br(2) = 180°, Fig. 5) in contrast to the angular structure observed in the salts of two-coordinate bromonium.

3.3. Complexes of the $CBr_4 \cdot 4AlBr_3$ system. For systems with this composition, we calculated ionic complex **10b** (Fig. 5) of the $[CBr_2]^{2+}$ dication with two $Al_2Br_7^-$ anions. In this symmetrical complex (D_2 symmetry), each bromine atom of the dication is linked to the terminal bromine atoms of two $Al_2Br_7^-$ anions *via* the $Br^{\delta+}...Br^{\delta'-}$ ionic bonds. Changes in the structure of the $[CBr_2]^{2+}$ dication produced by these ionic bonds are even smaller than those observed in complex **10a** (Fig. 5). The C—Br bond length changes only by 0.029 Å compared to that in the free dication. The electron density transfer to the dication is also smaller. As a result, the charges on the bromine atoms of the dication (0.94) are even larger than that in complex **10a**.

3.4. Complexes of the $CF_4 \cdot AlF_3$ and $CF_4 \cdot 2AlF_3$ systems. The $F_3CF{\rightarrow}AlF_3$ donor-acceptor complex (**11a**, Fig. 6) with a very weak and long F→Al bond (Wiberg indices are small, the energy of the cleavage (Δ_1) of this bond is only 0.8 kcal mol^{-1}) corresponds to the absolute minimum on the potential energy surface of the $CF_4 \cdot AlF_3$ system. In the case of the $CF_4 \cdot 2AlF_3$ system, the absolute minimum on the potential energy surface also corresponds to the $F_3CF{\rightarrow}AlF_2—F—AlF_3$ donor-acceptor complex (**11b**, Fig. 6). In this case, the F→Al donor-acceptor bond is shorter and stronger than that in complex **11a**; the energy of its cleavage (Δ_3) is 3.8 kcal mol^{-1}.

As expected, the minima that correspond to the structures with the $F^{\delta+}...F^{\delta'-}$ ionic bond were not found on the potential energy surface of the $CF_4 \cdot nAlF_3$ system (n = 1 or 2). The minima corresponding to the ionic complexes of the CF_3^+ carbenium cation with the AlF_4^- and $Al_2F_7^-$ anions [($F_3C^+...F—AlF_3^-$) or ($F_3C^+...FAlF_2—F{\rightarrow}AlF_3^-$)] were also not found. Optimization of structures of the complexes of this type with the initial geometry corresponding to separate CF_3^+ and AlF_4^- (or $Al_2F_7^-$) fragments and with the distance between their C and F atoms larger than 2.5 Å gives donor-acceptor complexes **11a** and **11b**. Therefore, unlike the $CX_4 \cdot nAlX_3$ systems (X = Br), in the case of X = F, only donor-acceptor complexes occur.

* * *

Our calculations demonstrated that of the $[CH_kX_{3-k}]^+$ cations and the $[CH_kX_{2-k}]^{2+}$ dications (X = Hal), only fluorine-containing compounds may be considered as carbenium ions. Electronic structures of cations containing atoms of other halogens are similar, and we studied these structures using X = Br as an example. Calculations demonstrated that not only in the CBr_4 molecule but also in the CBr_3^+ cation and even in the CBr_2^{2+} dication, are the charges on the carbon atoms negative (−0.40, −0.28, and −0.07).

The differences in the charge distribution in fluoromethanes, their $[CF_3]^+$ and $[HCF_2]^+$ cations and $[CF_2]^{2+}$ and $[HCF]^{2+}$ dications, on the one hand, and in analogous compounds containing Cl, Br, or I, on the other, result in different types of complexes formed from polyhalomethanes under the action of aluminum halides. In the $CF_4 \cdot nAlF_3$ systems (n = 1 or 2), only donor-acceptor complexes with a very weak F→Al bond and quite insignificant changes in the charge distribution compared to those in initial CF_4 and AlF_3 molecules are formed. By contrast, for the $CBr_4 \cdot nAlBr_3$ systems (n = 1, 2, or 4), local minima that correspond to highly electrophilic structures with cationic (CBr_3^+) and dicationic (CBr_2^{2+}) fragments were found on the potential energy surface in addition to the minima corresponding to donor-acceptor complexes.

In the donor-acceptor complexes of carbon tetrabromide (n = 1 or 2), the electron density on the carbon atom increases, even if very slightly, rather than decreases. The electron density more substantially increases in the ionic complexes of the CBr_3^+ cation and, particularly, of the CBr_2^{2+} cation with the $AlBr_4^-$ and $Al_2Br_7^-$ dianions. These results do not allow us to conclude that the electrophilicities of carbon atoms of halomethanes increase upon complexation with aluminum bromide.

Positive charges in bromomethanes are located on bromine atoms rather than on carbon atoms. In the donor-acceptor complexes, the charges on bromine atoms increase insignificantly. In the ionic adducts, as well as in free cations and dications, positive charges are located on bromine atoms and are equal to 0.39, 0.66, and 0.94 in cationic form **9a** and in dicationic structures **10a** and **10b**, respectively. An essential characteristic feature of these ionic complexes is the fact that the positively charged bromine atoms bonded to the carbon atom and the negatively charged bromine atoms of the $AlBr_4^-$ (or $Al_2Br_7^-$) anion are involved in the formation of these ionic bonds.

Cations and dications with one-coordinate and positively charged halogen atoms may be considered as halenium ions different from the known halonium ions containing dicoordinate halogen atoms. It is these highly electrophilic cationic and dicationic complexes that could be responsible for the superacidic properties of the $CBr_4 \cdot nAlBr_3$ systems. Note, however, that the thermodynamic conditions of their formation are very unfavorable. Actually, the formation of cationic and dicationic complexes from initial molecules requires more than 25 kcal mol^{-1} and 90 kcal mol^{-1}, respectively. This means that the relative equilibrium concentration of cationic and dicationic complexes is less than 10^{-18} and 10^{-60}, respectively.

An analogous situation was discussed in the review by Olah,[9] where the H_4O^{2+} dication was considered, the occurrence of which in protic superacids is indicated by the data of deuterium exchange, whereas an attachment of the proton to the H_3O^+ hydroxonium with the formation of the H_4O^{2+} dication requires about 60 kcal mol^{-1}. Considering this problem, Olah pointed to the fact that effects of solvation and, generally, clustering may play an important role shifting the superelectrophile to the thermodynamically more favorable region.

This work was supported by the International Science Foundation (Grant MRA 000) and the Russian Foundation for Basic Research (Project No. 93-03-04556).

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Received June 7, 1995;
in revised form September 8, 1995