Superelectrophiles generated in mBr$_2$·nAlBr$_3$ systems

Anatolii L. Chistyakov,* Ivan V. Stankevich, Irena S. Akhrem, Nina P. Gambaryan and Mark E. Vol'pin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation.
Fax: +7 095 135 5085; e-mail: stan@ineos.ac.ru

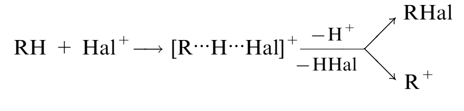
MNDO/PM3 calculations have proved the possibility of the existence in mBr$_2$·nAlBr$_3$ systems of highly electrophilic complexes with bidentate coordination of AlBr$_4^-$ anions with a positively charged (up to +1.45 a.u.) Br atom.

Organohalides play a key role in organic synthesis. The incorporation of halogens in unsaturated, aromatic and activated saturated hydrocarbon molecules is realised by the direct action of halogens without or in the presence of Lewis and protic acids.[1] The area of substrates for ionic halogenation by halogens in the presence of aprotic and protic acids has also been extended to alkanes.[2–5]

Recently, a quite novel application of Hal$_2$·nAlX$_3$ (Hal = Cl, Br, I; X = Br or Cl) systems was demonstrated. These systems turned out to be active initiators for n-alkane cracking at room temperature.[6] It is important in this case that ion-carbenium type reactions occur instead of halogenation. As a result, the transformation of alkanes into low isoalkanes and a mixture of oligomers proceeds.[6]

The attack of positively charged halogen-containing species on a hydrocarbon seems to be the key-stage in the halogenation of unsaturated and saturated hydrocarbons as well as in alkane cracking under the action of halogen in the presence of Lewis acids.[2–4,6] As a result of this attack, direct halogenation of the hydrocarbon or generation of a carbocation (from alkanes) followed by its subsequent transformation occurs.

Schematically these reactions can be presented as follows:



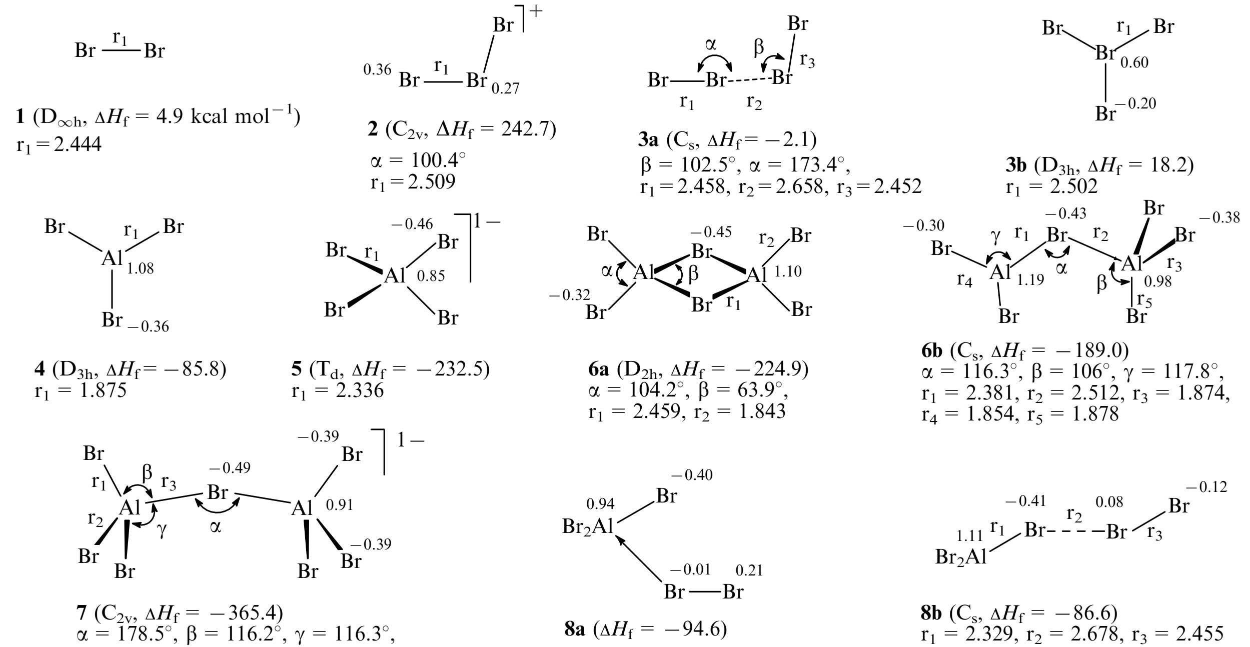
$$\mathrm{RH + Hal^+ \longrightarrow [R\cdots H\cdots Hal]^+ \xrightarrow[-HHal]{-H^+} RHal,\ R^+}$$

The nature of the positively charged halogen-containing species formed in the reactions of halogens with Lewis acids is not clear in spite of a number of investigations devoted to this problem.[7–14] The species generated under the action of aluminum halides on halogens has not been previously studied.

The linear dependence of the activity of Br$_2$·nAlBr$_3$ systems in octane cracking upon AlBr$_3$ content in these systems[6] probably means that species containing a highly charged halogen atom are made up of several molecules of AlBr$_3$ per molecule of halogen. In order to provide a background to any mechanistic interpretation of the reactions of hydrocarbons with halogenes in the presence of aluminum halides we have undertaken a quantum-chemical simulation of the molecular and electronic structure of the species that can be formed in Br$_2$·AlBr$_3$ and Br$_4$·nAlBr$_3$ (n = 1–4) systems. Particular attention has been paid to the search of superelectrophilic complexes that can play a key role in the electrophilic activation of saturated hydrocarbons.

The calculations were performed by the MNDO/PM3 method[15] with geometry optimization. The types of extremum points of the potential energy surfaces were determined from an analysis of the conforming Gessian-matrix eigenvalues. The basic structural and energy characteristics of Br$_2$ **1**, the cation Br$_3^+$ **2**, the angular dimer Br$_4$ **3a**, the trigonal dimer Br$_4$ **3b**, aluminum bromide **4**, anion AlBr$_4^-$ **5**, the dimer of aluminum bromide **6a**, the coordinatively unsaturated dimer of aluminum bromide **6b** and anion Al$_2$Br$_7^-$ **7** are given in Figure 1. Calculations on **1**–**7** were made previously by different semi-empirical methods of the MNDO type.[15] We repeated the MNDO/PM3 calculations of these systems because the values of effective charges on atoms (which are essential for our purposes) were not reported.

In Br$_2$·AlBr$_3$ systems the local minima on the potential energy surface (PES) of AlBr$_5$ were found as a result of a full optimization of its geometry. The major minimum corresponds to the donor–acceptor complex Br$_2$·AlBr$_3$ **8a**. In this complex the Br–Br bond is longer than the interatomic distance in the molecule Br$_2$ **1** by only 0.03 A. Changes in the AlBr$_3$-fragment geometry are also unimportant. Charge



1 (D$_{\infty h}$, ΔH_f = 4.9 kcal mol^{-1})
r$_1$ = 2.444

2 (C$_{2v}$, ΔH_f = 242.7)
α = 100.4°
r$_1$ = 2.509

3a (C$_s$, ΔH_f = −2.1)
β = 102.5°, α = 173.4°,
r$_1$ = 2.458, r$_2$ = 2.658, r$_3$ = 2.452

3b (D$_{3h}$, ΔH_f = 18.2)
r$_1$ = 2.502

4 (D$_{3h}$, ΔH_f = −85.8)
r$_1$ = 1.875

5 (T$_d$, ΔH_f = −232.5)
r$_1$ = 2.336

6a (D$_{2h}$, ΔH_f = −224.9)
α = 104.2°, β = 63.9°,
r$_1$ = 2.459, r$_2$ = 1.843

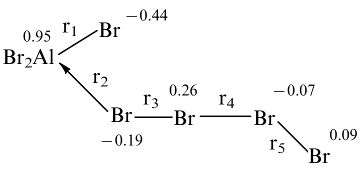
6b (C$_s$, ΔH_f = −189.0)
α = 116.3°, β = 106°, γ = 117.8°,
r$_1$ = 2.381, r$_2$ = 2.512, r$_3$ = 1.874,
r$_4$ = 1.854, r$_5$ = 1.878

7 (C$_{2v}$, ΔH_f = −365.4)
α = 178.5°, β = 116.2°, γ = 116.3°,
r$_1$ = 1.855, r$_2$ = 1.854, r$_3$ = 2.456

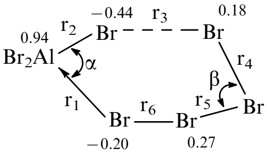
8a (ΔH_f = −94.6)

8b (C$_s$, ΔH_f = −86.6)
r$_1$ = 2.329, r$_2$ = 2.678, r$_3$ = 2.455

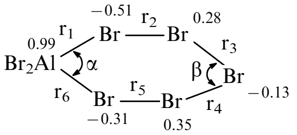
Figure 1



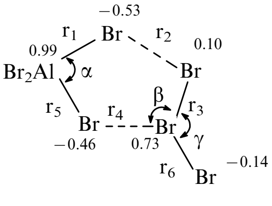
9a (C_s, $\Delta H_f = -113.5$)
$r_1 = 1.921$, $r_2 = 2.511$, $r_3 = 2.510$
$r_4 = 2.619$, $r_5 = 2.459$



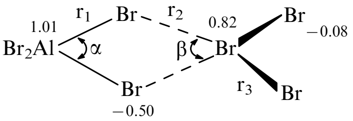
9b (C_1, $\Delta H_f = -114.3$)
$\alpha = 77.4°$, $\beta = 93.8°$, $r_1 = 2.505$,
$r_2 = 1.924$, $r_3 = 3.740$, $r_4 = 2.465$,
$r_5 = 2.616$, $r_6 = 2.513$



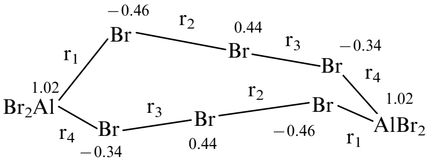
10 (C_1, $\Delta H_f = -129.7$)
$\alpha = 70.5°$, $\beta = 64.4°$, $r_1 = 2.404$,
$r_2 = 2.641$, $r_3 = 2.491$, $r_4 = 2.608$,
$r_5 = 2.546$, $r_6 = 2.468$



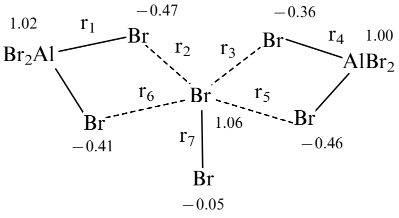
11a (C_s, $\Delta H_f = -114.8$)
$\alpha = 71.4°$, $\beta = 130°$, $\gamma = 100.7°$,
$r_1 = 2.422$, $r_2 = 2.736$, $r_3 = 2.510$,
$r_4 = 2.607$, $r_5 = 2.435$, $r_6 = 2.483$



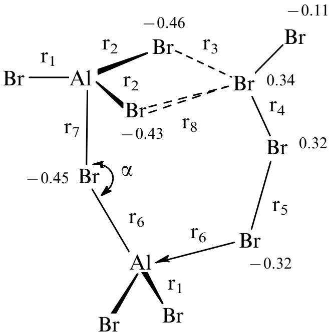
11b (C_{2v}, $\Delta H_f = -112.3$)
$\alpha = 71.2°$, $\beta = 65.7°$, $r_1 = 2.430$,
$r_2 = 2.607$, $r_3 = 2.490$



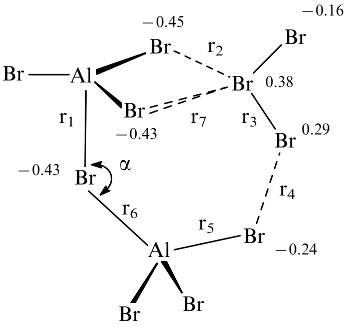
12 ($\Delta H_f = -255.4$)
$r_1 = 2.446$, $r_2 = 2.583$, $r_3 = 2.258$,
$r_4 = 2.462$



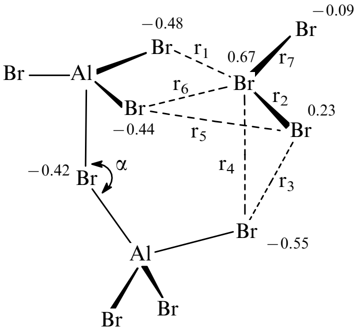
13 (C_1, $\Delta H_f = -236.9$)
$r_1 = 2.422$, $r_2 = 2.612$, $r_3 = 2.583$, $r_4 = 2.457$,
$r_5 = 2.584$, $r_6 = 2.557$, $r_7 = 2.500$



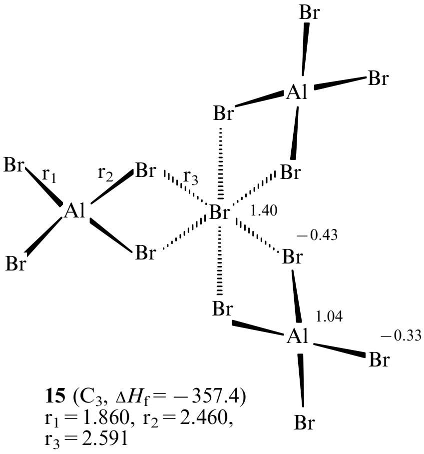
14a (C_1, $\Delta H_f = -246.1$)
$\alpha = 153.8°$, $r_1 = 1.85$, $r_2 = 2.37$, $r_3 = 2.69$,
$r_4 = 2.59$, $r_5 = 2.56$, $r_6 = 2.460$, $r_7 = 2.443$,
$r_8 = 2.67$



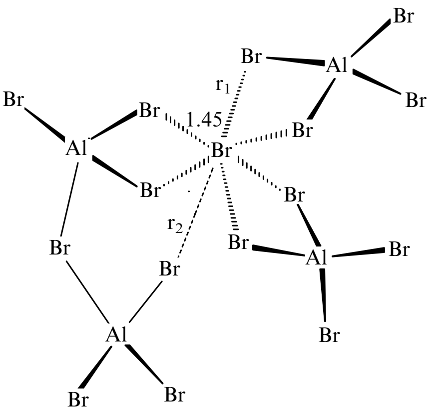
14b (C_1, $\Delta H_f = -237.8$)
$\alpha = 129.8°$, $r_1 = 2.448$, $r_2 = 2.70$,
$r_3 = 2.58$, $r_4 = 2.55$, $r_5 = 2.47$,
$r_6 = 2.46$, $r_7 = 2.67$



14c (C_1, $\Delta H_f = -236.3$)
$\alpha = 76.1°$, $r_1 = 2.65$, $r_2 = 2.52$, $r_3 = 2.75$,
$r_4 = 2.72$, $r_5 = 2.74$, $r_6 = 2.66$, $r_7 = 2.48$



15 (C_3, $\Delta H_f = -357.4$)
$r_1 = 1.860$, $r_2 = 2.460$,
$r_3 = 2.591$



16 ($\Delta H_f = -469.5$)
$r_1 = 2.6$, $r_2 = 2.72$

Figure 1

redistribution upon complexation is more appreciable. However, the positive charge on the terminal Br atom is not great (+0.21 a.u.). The heat of formation of **8a** is equal to −94.6 kcal mol^{-1}. The dissociation of this complex into Br_2 and $AlBr_3$ fragments requires nearly 14 kcal mol^{-1}.† However, the reaction of formation of complex **8a** from dimeric Br_4 **3a** and Al_2Br_6 **6a** is endothermic.

$$Br_4 + Al_2Br_6 \longrightarrow 2(Br_2{\cdot}AlBr_3) + 2\Delta_1 \qquad \Delta_1 = -19 \text{ kcal mol}^{-1}$$

The second higher local minimum corresponds to the complex $Br_2{\cdot}BrAlBr_2$ **8b**. In this complex the bond between the slightly positive Br of the Br_2 fragment and the Br of $AlBr_3$ fragment with a greater negative charge is rather weak. The heat of formation of this complex is equal to −86.6 kcal mol^{-1}. The dissociation energy is 5.7 kcal mol^{-1}.

On the PES there is no local minimum conforming to an ionic structure of $Br_2{\cdot}AlBr_3$. Indeed, the optimization of the geometry of $Br_2{\cdot}AlBr_3$ leads to the donor–acceptor complex **8a**, even if the initial Br–Br distance is large (from 2.7 to 3.0 A) and the Br–Al distance is small (1.9–2.2 A). Thus, complexes with a substantial charge on the Br atoms are not generated in the $Br_2{\cdot}AlBr_3$ system.

---

† 1 cal = 4.184 J

A different situation was observed for $Br_4{\cdot}nAlBr_3$ (n = 1–4) systems. In the system $Br_4{\cdot}AlBr_3$, the local minima on the PES were found to correspond to two rotamers of the donor–acceptor complex between the angular molecule Br_4 **3a** and $AlBr_3$ **4**. One of these rotamers is transoid **9a** and the other is cisoid **9b** with regard to the positions of the terminal atom of Br_4 fragment and the aluminum group. The geometric changes of Br_4 and $AlBr_3$ upon the complexation are insignificant. The changes in charge distribution in $AlBr_3$ are small, too. The redistribution of electron density on the Br_4 fragment is more noticeable: the Br–Br bond of the donor atom Br in the transoid rotamer **9a** is polarized. In the cisoid rotamer **9b** the positive charge on the terminal Br atom of the Br_4 fragment also appears. The electrostatic interaction between this positive Br and the negatively charged Br of the $AlBr_3$ group brings together these atoms and diminishes the angle α in the Br_4 fragment from 102.5° to 93.8°. This slightly stabilizes the cisoid rotamer relative to the transoid one (the energy difference is equal to 0.8 kcal mol^{-1}).

The major minimum on the PES corresponds to complex **10**. This system is formed as the result of further diminution of the angle α in the Br_4 fragment of the cisoid rotamer **9b**. The potential barrier to this transformation is equal to 2.2 kcal mol^{-1}. An almost planar, six-membered cycle, with more equalized bond lengths than in the cisoid rotamer, is contained in complex **10**. In particular, the distance between the electrostatically interacting Br atoms is much contracted, and the Al–Br bond length, which is in the cycle, is greatly increased. The charges on cycle atoms alternate strongly and the maximal charge on Br atoms reaches +0.35 a.u.

In the search for species with large positive charges on the Br atoms we have used two initial approaches. Fragments of the PES were investigated in the range of interaction both of $AlBr_3$ **4** with the trigonal molecule Br_4 **3b**, in which charge on the central Br is equal to 0.6 a.u., and of the anion $AlBr_4^-$ **5** with the cation Br_3^+ **3**.

As a result, two local minima conforming to complexes **11a** and **11b** were found. Complex **11a** contains the planar five-membered cycle, $AlBr_4$. It can be described as the ionic complex between the anion $AlBr_4^-$ and the cation Br_3^+. In this complex the negatively charged Br atoms of the anion are coupled with the central and terminal Br atoms of Br_3^+. This description is made on the grounds of analysis of both the one-electron density matrix and the distances between atoms of the cycle. The maximal positive charge on the Br atom of this complex is equal to 0.72 a.u. An even greater positive charge is found on the central atom of the cation Br_3^+ when it is bidentately coordinated with Br atoms of the anion $AlBr_4$. Such coordination is realized in complex **11b**, where the positive charge on Br reaches a value of +0.82 a.u. The energy difference between the two complexes **11a** (−114.8) and **11b** (−112.3 kcal mol^{-1}) is small. The potential barrier of transition from complex **11b** to **11a** is also small (1.1 kcal mol^{-1}). Thus, the transitions between mono- and bidentate forms of the ionic complexes are as easy as the transitions between the rotamers **8a** and **8b** of the donor–acceptor complexes. The energies of the donor–acceptor complexes and of the ionic ones are nearly the same (the heats of formation of the cisoid **9b** and transoid **9a** rotamers are −114.3 and −113.5 kcal mol^{-1}; and those of the mono- **11a** and bidentate **11b** ionic complexes are −114.8 and −112.3 kcal mol^{-1}, respectively). The energy of all these complexes is above the energy of the major minimum conforming to complex **10** by roughly 15 kcal mol^{-1}.

Thus, two local minima on the PES of $Br_4{\cdot}AlBr_3$ were found that correspond to complexes containing highly electrophilic Br atoms with charges equal to 0.72 and 0.82 a.u., respectively. It must be noted that the energies of these complexes are above the energy of the major minimum by 15 kcal mol^{-1} only.

The system $Br_4{\cdot}2AlBr_3$ has a main minimum on its PES ($\Delta_f H^\circ$ = −255.4 kcal mol^{-1}) which corresponds to complex **12**. This complex can be considered as a product of the tail–head dimerization of complexes **8a** or **8b**. The dimerization occurs both as a result of the electrostatic interaction between the terminal Br atoms (q_{Br} = +0.21 a.u.) of the donor–acceptor complexes **8a** and the negatively charged (q_{Br} = −0.40 a.u.) Br atoms bound with aluminum or, by the donor–acceptor interaction between the terminal Br atoms of the electrostatic complexes **8b** and Al atoms.The complex **12** contains an eight-membered cycle with two nearly linear Br_3 fragments. The positive charges, equal to 0.44 a.u., are concentrated on each of the central atoms of these linear fragments.

A complex with a large positive charge on a Br atom was found when two $AlBr_3$ **4** groups were put into closer contact with two negatively charged Br of the trigonal Br_4 **3b**. A conforming local minimum is found to be higher than the main one by 18.5 kcal mol^{-1}. In this complex **13** a bidentate coordination of two anions $AlBr_4^-$ **5** on positively charged Br atom in the dication fragment $Br{-}Br^{2+}$ is realized. The charge on this atom in **13** is equal to +1.06 a.u. (the total charge on each $AlBr_4^-$ group is equal to −0.5 a.u.). The skeleton of the complex **13** is practically planar. Therefore nothing can hamper the attack of the electrophilic atom of complex **13**.

The composition of the system $Br_4{\cdot}Al_2Br_6$ is the same as that of the preceding one. The formation of complexes in this system does not need the dissociation of the dimer of aluminum bromide. Therefore, one could expect that conforming complexes would be more stable than the above mentioned. However, it was found that the main energy minimum on the PES of the above system (complex **12**, −255.4 kcal mol^{-1}) is deeper than the major minimum on the PES of $Br_4{\cdot}Al_2Br_6$ system (**14a**, −246.1 kcal mol^{-1}). The donor–acceptor complex **14a** between the angular molecule **3a** and the coordinatively unsaturated unsymmetrical dimer $Br_2AlBrAlBr_3$ **6b** corresponds to this minimum. The first atom of the Br_4 fragment of this complex is bonded with the unsaturated Al atom by the donor–acceptor bond and the angular atom of the Br_4 fragment is linked with the negatively charged terminal Br atoms of the dimer **6b**. This additional electrostatic interaction increases the energy of dissociation of complex **14a** in comparison with complex $Br_2{\cdot}AlBr_3$ **8a**, which has the donor–acceptor interactions only (55.0 and 13.7 kcal mol^{-1}, respectively).

The second local energy minimum (by 8.3 kcal mol^{-1} above the first one) corresponds to the complex **14b** which is topologically similar to the complex **14a**. The geometrical modifications of complex **14b** permit one to interpret this complex as an ionic one with electrostatic interaction between the cation Br_3^+ **2** and the anion $Al_2Br_7^-$ **7**. The electrostatic interaction between the central atom of the cation with Br atoms of the terminal group of the anion $Al_2Br_7^-$ is bidentate, whereas the interaction between the terminal atom of the cation and the other terminal group of anion is monodentate. It should be emphasized that in spite of such an ionic description there are no Br atoms with substantial positive charges in this complex.

The third complex **14c** differs from **14a** and **14b** in its orientation of the cationic Br_3^+ fragments. It is curious that this produces a significant increase in the positive charge on the central atom of the cation. The bidentate coupling with the central atom of the cation in complex **14c** is realized in the cation plane and not at an angle to it. The terminal Br atoms interact electrostatically both with the terminal atom of the cation and with the central one. The charge on this central atom is equal to 0.67 a.u. and nothing restricts access to it. The energy of this complex is equal to −236.3 kcal mol^{-1} and differs slightly from that of complex **14b** (by 1.5 kcal mol^{-1}).

In the system $Br_4{\cdot}3AlBr_3$ the local minimum on its PES conforms to complex **15** with a substantial positive charge on the Br atom. This atom interacts electrostatically with three anionic $AlBr_4^-$ groups. The interaction with each of these groups is bidentate and the complex has a propeller-type shape. The charge on the central Br atom is equal to 1.4 a.u., so complex **15** can be a superelectrophile. The flattening of the complex requires 12.7 kcal mol^{-1} only. That is why its propeller-type shape does not decrease the reactivity of the complex to any great extent. The local energy minimum conforming to this complex (-357.4 kcal mol^{-1}) is above the major one (-366.8 kcal mol^{-1}) by 9.4 kcal mol^{-1}.

In the $Br_4{\cdot}4AlBr_3$ system the charge on the cenral Br atom in the propeller-type complex **16** is yet greater ($+1.45$ a.u.). Complex **16** differs from **15** by replacement of one anionic group $AlBr_4^-$ by the anion $Al_2Br_7^-$. This anion is curved so that its terminal Br atom interacts with the central atom electrostatically. The heat of formation of this complex (-469.5 kcal mol^{-1}) is greater than that of the main isomer (-496.2 kcal mol^{-1}) by 26.7 kcal mol^{-1}.

Thus, as a result of the MNDO/PM3 calculations, complexes with a substantial positive charge on a Br atom were found. These are complexes **11a**, **11b**, **13**, **14c**, **15** and **16**. It is in the complexes with a bidentate coordination of anions to the central atom where the positive charges on this atom are especially great. Maximal charge on the Br atom is equal to 0.82 in the case of the coordination of one anion (**11b**). In the case of coordination of two anions the charge is increased to 1.06 a.u. (**13**). In complexes **15** and **16**, where three anions are coordinated to the central atom, this charge amounts to 1.4 and 1.45 a.u., respectively. The reactions of formation of all these complexes from dimeric Br_4 and Al_2Br_6 are exothermic (with the exception of complex **11b**; the reaction of formation of this complex is endothermic, but its formation requires only 2.25 kcal mol^{-1}).

The energies of complexes **11a** and **11b** are above the energy of the main minimum by 15 kcal mol^{-1} only. In the cases of complexes **13** and **14c** this difference is equal to 20 kcal mol^{-1}. The energies of complexes **15** and **16** are greater than the energies of the main complexes by 9.7 and 26.7 kcal mol^{-1}, respectively. Consequently, the energy characteristics of the complexes found are favorable for their formation. Also, the electrophilic centres of these systems are accessible to attack. Therefore, these complexes can play a key role in the electrophilic activation of hydrocarbons. Such complexes have not been considered earlier as possible intermediates of the reactions of halogens with hydrocarbons in the presence of aluminum bromide.

References

1 (*a*) H. B. Brachdlin and E. T. McBeein, in *Friedel–Crafts and Related Reactions*, ed. G. A. Olah, Wiley-Interscience, New York, 1964, Part 2; (*b*) G. H. Schmid and D. G. Garrat, in *The Chemistry of Double-Bonded Functional Groups*, ed. S. Patai, Wiley, New York, 1977, Suppl. A., Part 2, p. 725; (*c*) P. B. D. De la Mare and R. Bolton, in *Electrophilic Additions to Unsaturated Systems*, Elsevier, New York, 1982, pp. 136–197; (*d*) K. A. Vyunov and A. I. Ginak, *Usp. Khim.*, 1981, **50**, 273 (*Russ. Chem. Rev.*, 1981, **50**, 151); (*e*) M. F. Ruasse, *Acc. Chem. Res.*, 1990, **23**, 87.

2 G. A. Olah, R. Renner, P. Schilling and Y. K. Mo, *J. Am. Chem. Soc.*, 1973, **95**, 7686.

3 I. S. Akhrem, A. V. Orlinkov, S. V. Vitt, L. V. Afanas'eva and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2028 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1864).

4 I. S. Akhrem, A. V. Orlinkov, L. V. Afanas'eva, E. I. Mysov and M. E. Vol'pin, *Tetrahedron Lett.*, 1995, **36**, 9365.

5 Y. Halpern, *Isr. J. Chem.*, 1975, **13**, 99.

6 I. S. Akhrem, L. V. Afanas'eva, A. V. Orlinkov and M. E. Vol'pin, *Mendeleev Commun.*, 1994, 131.

7 *Bromine Compounds Chemistry and Application*, eds. D. Price, B. Iddon and B. J. Wakefield, Elsevier, Amsterdam, 1988.

8 (*a*) R. S. Brown, H. Slebocka-Tilk, A. J. Bennet, G. Bellucci, R. Bianchini and R. Ambrosetti, *J. Am. Chem. Soc.*, 1990, **112**, 6310 and references therein; (*b*) R. W. Nagorski and R. S. Brown, *J. Am. Chem. Soc.*, 1992, **114**, 7773 and references therein.

9 O. M. E. El-Dusouqui, K. A. M. Mahmut and J. Sultab, *Tetrahedron Lett.*, 1987, 2178.

10 G. A. Olah, *Acc. Chem. Res.*, 1987, **20**, 422.

11 G. A. Olah and L. Heiliger, *J. Am. Chem. Soc.*, 1990, **112**, 3920.

12 Y. Li, X. Wang, F. Jensen, K. N. Houk and G. A. Olah, *J. Am. Chem. Soc.*, 1990, **112**, 3922.

13 (*a*) R. J. Gillespie, R. Kapoor, R. Faggiani, C. J. L. Lock, M. Murchie and J. Passmore, *J. Chem. Soc., Chem. Commun.*, 1983, 8; (*b*) R. Faggiani, R. J. Gillespie, R. Kapoor, C. J. L. Lock and J. E. Vekris, *Inorg. Chem.*, 1988, **27**, 4350.

14 (*a*) K. Kimura, T. Jamazaki and J. Ashiba, *Chem. Phys. Lett.*, 1978, **58**, 104; (*b*) D. M. De Leeuw, R. Mooyman and G. A. De Lange, *Chem. Phys. Lett.*, 1978, **54**, 231.

15 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209, 221.

Received: Moscow, 14th March 1996
Cambridge, 28th May 1996; Com. 6/02085B