

The summary of Marzena Marchaj Ph.D. thesis titled: "*The influence of the superhalogen anions stability on the selected physicochemical processes*"

Negatively charged molecular systems play an important role in many various physicochemical processes (both as the reagents and reaction products). Due to their numerous applications in material and environmental chemistry, certain types of molecular anions are the subject of continuing experimental and theoretical studies. Superhalogen anions are among those whose unusual properties attract attention, as their extremely large electronic stabilities may cause important chemical consequences. Since the superhalogen anions are the anionic daughters of their corresponding neutral superhalogen molecules, the oxidizing abilities of the latter should be significant. Namely, the neutral superhalogens, due to their large tendency to accept an excess electron, are expected to be capable of withdrawing a substantial amount of electron density from other systems. Hence, the superhalogens might be considered as the effective oxidizers even with respect to the compounds exhibiting large ionization potentials.

The main goal of this Ph.D. thesis was to demonstrate that the electronic and thermodynamic stability of a superhalogen anion is the most important factor determining its usefulness in designing novel salts and inducing certain chemical reactions. Namely, a commonly accepted  $(MX_{k+1})^-$  formula (defining presumably stable superhalogen anions) may lead to unstable systems in some cases. On the other hand, as demonstrated for stable species, the magnitude of its electron binding energy plays the key role in the stability of the final product formed as the result of the superhalogen system interacting with other compound. In addition, the role of superhalogens as the trigger compounds capable of initiating radical substitution reactions was presented.

The results (described in four publications) might be summarized as follows:

- (i) The  $\text{SiF}_5^-$ ,  $\text{SiCl}_5^-$ ,  $\text{GeF}_5^-$ , and  $\text{GeCl}_5^-$  anions are electronically, geometrically, and thermodynamically stable species adopting the  $D_{3h}$ -symmetry trigonal bipyramidal equilibrium structures whereas the  $\text{CF}_5^-$  and  $\text{CCl}_5^-$  systems do not exist in the elevated temperatures due to their thermodynamic instability (susceptibility to the fragmentations leading to the either  $\text{F}^-$  or  $\text{Cl}^-$  loss). The  $\text{MX}_5^-$  ( $\text{M}=\text{Si, Ge}$ ;  $\text{X}=\text{F, Cl}$ ) systems are strongly bound superhalogen anions whose vertical electron binding energies are 9.316 eV ( $\text{SiF}_5^-$ ), 6.196 eV ( $\text{SiCl}_5^-$ ), 9.742 eV ( $\text{GeF}_5^-$ ), and 6.452 eV ( $\text{GeCl}_5^-$ ), while the formation of only weakly bound  $\text{CX}_4\cdots\text{X}^-$  ( $\text{CF}_4\cdots\text{F}^-$  and  $\text{CCl}_4\cdots\text{Cl}^-$ ) anionic complexes might be expected when the carbon atom plays a central atom role.
- (ii) The  $\text{LiF}_3^-$ ,  $\text{NaF}_3^-$ ,  $\text{KF}_3^-$ ,  $\text{BeF}_4^-$ ,  $\text{MgF}_4^-$ ,  $\text{CaF}_4^-$ ,  $\text{BF}_5^-$ ,  $\text{AlF}_5^-$ , and  $\text{GaF}_5^-$  (designed using the  $\text{MF}_{k+2}^-$  formula) are geometrically and electronically stable anionic systems characterized by large vertical electron detachment energies. Some of the  $\text{MF}_{k+2}^-$  anions (i.e.,  $\text{BeF}_4^-$ ,  $\text{BF}_5^-$ ,  $\text{AlF}_5^-$ , and  $\text{GaF}_5^-$ ) are thermodynamically unstable species as they were found susceptible to the fluorine atom loss leading to the formation of the corresponding  $\text{MF}_{k+1}^-$  superhalogen anions. In contrast, the remaining negatively charged  $\text{MF}_{k+2}^-$  systems (i.e.,  $\text{LiF}_3^-$ ,  $\text{NaF}_3^-$ ,  $\text{KF}_3^-$ ,  $\text{MgF}_4^-$ , and  $\text{CaF}_4^-$ ) are predicted to be thermodynamically stable and not susceptible to any fragmentation reactions. The thermodynamic instability of the  $\text{BeF}_4^-$ ,  $\text{BF}_5^-$ ,  $\text{AlF}_5^-$ , and  $\text{GaF}_5^-$  systems might be caused by relatively large electron binding energies of the corresponding  $\text{MF}_{k+1}^-$  superhalogen fragmentation products. Even though the VDEs of the  $\text{MF}_{k+2}^-$  systems are usually slightly larger than the VDEs of their corresponding  $\text{MF}_{k+1}^-$  superhalogen anions, the  $\text{MF}_{k+2}^-$  systems do not appear to be promising strongly bound molecular anions in general, mostly due to the fact that their thermodynamic stability is jeopardized.



- (iii) The  $\text{BF}_4$  and  $\text{AlF}_4$  superhalogen molecules are capable of ionizing single  $\text{H}_2\text{O}$  molecule and small water clusters (up to the tetramer). The ability of ionizing  $(\text{H}_2\text{O})_n$  ( $n=1-4$ ) systems by these superhalogens is related to very large electron affinities characterizing  $\text{BF}_4$  and  $\text{AlF}_4$  molecules and to the significant vertical electron binding energies (8.98-9.79 eV) of their anionic daughters. Three evidences of the ionic nature of  $[(\text{H}_2\text{O})_n]^+[\text{BF}_4]^-$  and  $[(\text{H}_2\text{O})_n]^+[\text{AlF}_4]^-$  ( $n=1-4$ ) systems are provided: (a) the *geometrical evidence* that mainly consists in the presence of  $\text{H}_3\text{O}$  fragment (typical for the cationic water oligomers) in all water clusters assembled into the resulting systems, (b) the *energetic evidence* that is based on the large estimated binding energies (28-73 kcal/mol) between the water and superhalogen components, and (c) the *charge-flow evidence* consisting in the calculated substantial amount of electron density flow (0.53-0.83e) from  $(\text{H}_2\text{O})_n$  to the associated superhalogen counterpart molecule. Despite the results are limited to small water clusters ( $(\text{H}_2\text{O})_n$ ,  $n=1-4$ ), one may expect that the  $\text{BF}_4$  and  $\text{AlF}_4$  superhalogens ability of oxidizing (ionizing) such systems might be extended to cover water clusters of practically any size (due to the fact that the ionization potential of water cluster tends to decrease with increasing cluster size, hence the ionization of larger water systems is not expected to require stronger oxidizers).
- (iv) The  $\text{AlF}_4$  superhalogen may oxidize any methane chloro derivative (i.e.,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ ) to form an ionic  $(\text{CH}_{4-n}\text{Cl}_n)^+[\text{AlF}_4]^-$  compound (where  $n=1-4$ ). In the case of methane, however, the interaction with  $\text{AlF}_4$  leads to a weakly bound  $\text{CH}_4 \cdots \text{AlF}_4$  complex instead. The ionic nature of the  $(\text{CH}_3\text{Cl})^+[\text{AlF}_4]^-$ ,  $(\text{CH}_2\text{Cl}_2)^+[\text{AlF}_4]^-$ ,  $(\text{CHCl}_3)^+[\text{AlF}_4]^-$ , and  $(\text{CCl}_4)^+[\text{AlF}_4]^-$  systems is confirmed by their large binding energies (26.4-36.7 kcal/mol), considerable charge flow between the fragments (ca. 0.7e), and geometry relaxation of the constituting subunits. The ionic  $(\text{CH}_3\text{Cl})^+[\text{AlF}_4]^-$ ,  $(\text{CH}_2\text{Cl}_2)^+[\text{AlF}_4]^-$ ,  $(\text{CHCl}_3)^+[\text{AlF}_4]^-$ , and non-ionic  $\text{CH}_4 \cdots \text{AlF}_4$  systems, albeit locally geometrically stable, are expected to further evolve (via the proton transfer) to their more stable  $(\text{CH}_2\text{Cl})'(\text{HAlF}_4)$ ,  $(\text{CHCl}_2)'(\text{HAlF}_4)$ ,  $(\text{CCl}_3)'(\text{HAlF}_4)$ , and  $(\text{CH}_3)'(\text{HAlF}_4)$  radical counterparts, whereas the remaining  $(\text{CCl}_4)^+[\text{AlF}_4]^-$  system is predicted to represent the final product (due to the lack of hydrogen atoms). These findings allow to conclude that the  $\text{AlF}_4$  superhalogen may, in fact, react with methane and any of its chloro derivatives. These reactions should lead to the  $\text{HAlF}_4$  and  $(\text{CH}_{3-n}\text{Cl}_n)'$  final products ( $n=0-3$ ), excluding the  $\text{CCl}_4$  case (with the  $(\text{CCl}_4)^+[\text{AlF}_4]^-$  ionic system as the final product). Since it seems justified to anticipate that the  $(\text{CH}_2\text{Cl})'$ ,  $(\text{CHCl}_2)'$ ,  $(\text{CCl}_3)'$ , and  $(\text{CH}_3)'$  radicals may subsequently cause further reactions with the surrounding molecules (e.g., hydrocarbons), one may treat the  $\text{AlF}_4$  system as the trigger-compound that should initiate other processes. In other words, the  $\text{AlF}_4$  superhalogen is expected to act as a radical initiator which triggers the radical-substitution reaction chain (via the propagation process) when introduced to either methane or its chloro derivatives. In fact, this conclusion might be much more general (concerning other superhalogens and various hydrocarbons).