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Compounds of the Halogen Cations

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The conditions for the synthesis, the thermodynamics of the formation and decomposition, the structure, and the nature of the chemical bond in the halogen cations are examined. The electronic, vibrational, nuclear quadrupole resonance, and nuclear magnetic resonance spectra are analysed and questions concerning the practical application of the halogen cations as some of the most powerful oxidants, are discussed.
The bibliography includes 216 references.

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I. INTRODUCTION

The compounds of halogen cations are complexes with a singly charged cation $[Hal(Hal'_nHal''_m)]^+$, where Hal is the complex forming halogen (Cl, Br, I, or At) in the +3, +5, or +7 oxidation states, while Hal' and Hal'' are halogen ligands (ranging from F to At). The ligands can also be numerous interhalogen compounds and apparently pseudohalogens. Fluorine is the commonest ligand.

The term "halogen cations" was introduced by Arotsky and Symons[1] and has come to be widely used.[2-5] The first review of the chemistry of the halogen cations was published in 1962[1] and was followed by others.[4,6-9] During the period since the publication of the last review, the number of studies on the chemistry of the halogen cations has doubled and it became necessary to give a systematic account of the accumulated data and to describe more fully the studies by Soviet workers.

There is now no doubt that the complex forming agent in the cation $[Hal(Hal'_nHal''_m)]^+$ is always the most electropositive of the halogens. With increase of its electropositivity and also with increase of the strength of the Lewis acids from which the anions have been derived ($BF_3 < PF_5 < PtF_5 < SbF_5 < AsF_5$). the stability of the halogen cation compounds increases. The compounds of halogen cations are mainly ionic species with a certain amount of covalent character in the chemical bonds, which is manifested by the formation of halide bridge bonds between the cation and the anion. Extremely electrophilic cations, namely $[I_3]^+$, $[ICl_2]^+$, $[IF_6]^+$, $[ClF_2]^+$, etc., can exist only in media with very weak basic properties (superacids, SO_2, SbF_5, IF_5, etc). With weakly basic anions, such as $[SbF_6]^-$, $[AlCl_4]^-$, $[SbCl_6]^-$, etc., cations of this kind form crystalline phases.

The synthesis of the halogen cation compounds is based on the interaction of interhalogen compounds, halogens, or their mixtures with strong Lewis acids (acceptors of halogen atoms), for example in accordance with the mechanism

$$BrF_3+AsF_5=[BrF_2][AsF_6]\ .$$

On the other hand, if a strong Lewis base (a halogen atom donor) is introduced into the reaction instead of the Lewis acid, then representatives of another group of complexes, namely compounds of halogenate anions,[10-12] are formed from the solution, for example:

$$BrF_3+CsF=Cs[BrF_4]\ .$$

For this reason in solutions of interhalogen compounds, compounds of halogen cations and the halogenate anions interact as Lewis acids and bases:[6,13,14]

$$[BrF_2][AuF_4]+Ag[BrF_4]=Ag[AuF_4]+2BrF_3\ .$$

The chemistry of the halogen cation compounds is so far in the initial stage of its development. In this review, which is the first in the Soviet literature, an attempt is made to identify the most promising research trends and to describe the principal properties and reactions of the halogen cation compounds and the methods of their synthesis.

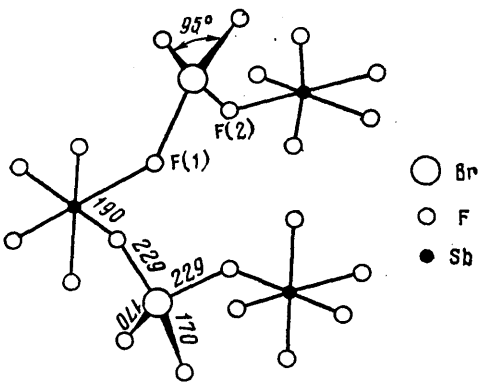


Figure 1. Schematic illustration of the structure of $[BrF_2]$. $[SbF_6]$ [17,18] (the interatomic distances are indicated in pm).

II. THE STRUCTURE AND NATURE OF THE CHEMICAL BOND

All the triatomic halogen cations, namely $[I(I)_2]^+$, $[BrF_2]^+$, $[ClF_2]^+$, and similar species, have a bent structure (Fig.1), in which the angle between the bonds is 91–103° (C_{2v} symmetry).[15-21] We may note that the triatomic halogenate anions, i.e. $[I_3]^-$, $[BrF_2]^-$, $[ICl_2]^-$, etc, are linear and

symmetrical.[10] With increase of the electronegativity of the central atom, its effective positive charge diminishes {δ = 1.48 for $[BrF_2]^+$ and 0.98 for $[ClF_2]^+$} and at the same time the effective charge of the ligands changes (from $\delta = -0.24$ to $\delta = 0.01$ for the same cations).[16,22-27] The effective charges on the central atom and the ligands in the cation $[Cl(ClF)]^+$ are respectively 0.324 and 0.338.[23-29] The values of δ quoted in the literature differ and depend on the methods of calculation. In particular, δ for Hal = I in the $[I_3]^+$ cation varies over the range 0.55–0.79.[15,30,31]

As in the triatomic halogenate anions, in the triatomic halogen cations only the *p* orbitals of the central atom and the ligands participate in the formation of the bond.[32] The population of the *d* orbitals in the $[I_3]^+$ and $[I_3]^-$ ions is insignificant and their involvement in bond formation is not obligatory. When an electron pair is removed from the $[I_3]^-$ anion with formation of the $[I_3]^+$ cation, the valence state of the central atom remains unchanged and only the degree of its oxidation increases.[32] An increase in the overall *f*-electron density on the complex-forming agent (iodine) compared with the free I^- ion has been noted but the complex-forming agent–ligand interatomic distance in the $[I_3]^+$ ion is the same as in gaseous iodine.

Under certain conditions, iodine atoms can produce the diamagnetic cation $[I_4]^{2+}$, which has no complex-forming agent[34-36] and the chain cations $[I_{15}]^{3+}$ (Fig.2). The latter cation consists of three $[I_5]^+$ ions linked to one another with the central atoms E(1), I(1), and E(2). The bond lengths in the ligands and in the gaseous iodine molecule are comparable, the smallest distance between the iodine atoms in neighbouring chains being 390.6 pm.[37] According to Chung and Cady,[38] the existence of the cation $[I_7]^+$ is doubtful.

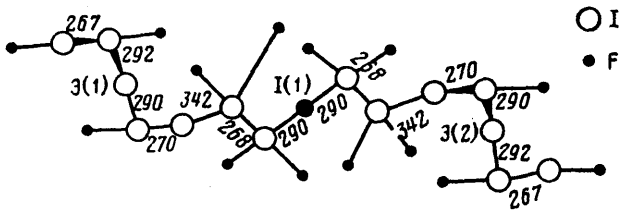


Figure 2. The configuration of the ion $[I_{15}]^{3+}$ [37] (the interatomic distances are given in pm): E(1), E(2), and I(1) are central atoms.

The angular structure of the cations $[ClF_2]^+$ and $[BrF_2]^+$ (Fig.1) corresponds best to the model comprising localised *p* orbitals with two covalent p_σ bonds.[16,22-26,39] The ligands of the cations together with the *cis*-bridging halogen atoms of the anion [F(1) and F(2), see Fig.1] form a deformed square. The sterically active unshared electron pairs of the complex-forming agent are in the *trans*-positions above and below the plane of the square (Fig.3*b*) and the cations are therefore classified as pseudohexacoordinated.[15,20,26,27] If the cation is regarded as a planar square, then the chemical bonds can be represented by two mutually perpendicular asymmetric four-electron semi-ionic p_σ bonds formed by the np_x and np_y orbitals of the central atom. The involvement of the *nd* orbitals is in this case insignificant and they are regarded[23,40] merely as having polarisation functions. For example, the population of the 3*d* orbital of the chlorine atom in the cation $[ClF_2]^+$ is only 0.05e.[40]

Fig.3 presents models of the valence bonds in the triatomic cations. When E = Cl or Br and X = Y = F, the interatomic X–X, Y–Y, and X–Y distances are 340, 230–250, and 270–280 pm respectively.[16] The E–X bond length increases, for the same complex-forming agent, on passing from X = Cl to X = I.[17,41] The E–Y bond order is 0.42–0.47.[42] The bond length ratio (E–X)/(E–Y) in the cations considered is 1.04–1.05 and diminishes with increase of the E–Y bond strength on passing from E = Cl to E = I.[8]

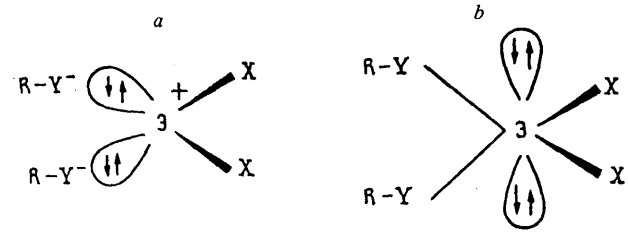


Figure 3. The planar ionic (*a*) and bridged (*b*) structures of the halogen cation compounds with an angular cation;[15,26] E = complex forming agent, X = ligands, and Y = bridging ligands of the anions.

With decrease of the bond angle in the cation, the degree of covalence of the bond between the complex-forming agent and the bridging ligand increases.[26] If the bridging ligands of the anions form strong bonds with the complex-forming agent in the cation, then all the electron pairs occupy octahedral sites with the angle between the bonds approximately 90°.[39,43] It is believed[27] that the strength of the covalent bond between the cation $[BrF_2]^+$ (Fig.1) and the anions increases from $[SbF_6]^-$ to $[GeF_6]^- \cong [Sb_2F_{11}]^-$.[23-25,27] Owing to the strong solvation of $[BrF_2]^+$ in liquid BrF_3, the Br–F bond length increases, which induces a shift of the ν_1 band in the Raman spectrum from 705–707 cm^{-1} to 625 cm^{-1}.[44] In the crystals of $[ICl_2][SbCl_6]$, the iodine atoms of the two ligands of the cation and the two bridging ligands are disposed virtually in the same plane, as in the structure of the anion $[ICl_4]^-$.[19,30,45]

The interhalogen compounds $[I(ICl)_2]^+$ (Fig.4)[46-48] and $[I(IBr)]^+$[48] can also serve as ligands in the cations. In the coordinated ICl and IBr molecules the bonds are shorter than in the single molecules. The anion $[SbCl_6]^-$ converts the cation $[I(ICl)]^+$ into a symmetrical ion, while the anion $[AlCl_4]^-$ converts it into an asymmetric ion.[48] The anion $[AlCl_4]^-$ alters also the interatomic distances in the ICl ligand: I(2)–Cl(1) ≠ I(3)–Cl(2). Nevertheless the cation remains planar (Fig.4).

The attempts[49,50] to represent the cation $[Cl(ClF)]^+$ as having a symmetrical structure in which the central atom is fluorine failed. Analysis of the vibrational spectra and quantum-mechanical calculations showed that this cation is asymmetric.[8,22]

Among the penta-atomic cations $[(Hal(Hal')_4]^+$, only compounds of the type $[HalF_4]^+$ (Hal = Cl, Br, or I) are so far known. They have a trigonal-bipyramidal structure (C_{2v} symmetry) with the unshared electron pair in the equatorial plane.[51-53] This structure has been confirmed by X-ray diffraction and NMR. Quantum-mechanical calculations lead to the C_{2v} symmetry only when the *d* orbital of the central

atom is used.[54,55] The hepta-atomic cations $[Hal(Hal')_6]^+$ are also known only with fluoride ligands. The octahedral structure of the cations $[ClF_6]^+$, $[BrF_6]^+$, and $[IF_6]^+$ has been explained either by the sp^3d^2 hybridisation of the atomic orbitals of the central atom or by the involvement of all of its three delocalised pairs of p electrons in the formation of three polar three-centre four-electron σ-bonds of the p–p type.[56,57] The high symmetry of the environment of the complex-forming agent has been confirmed by the analysis of ^{129}I Mössbauer,[58,59] NMR,[60,61] and vibrational spectra.[62]

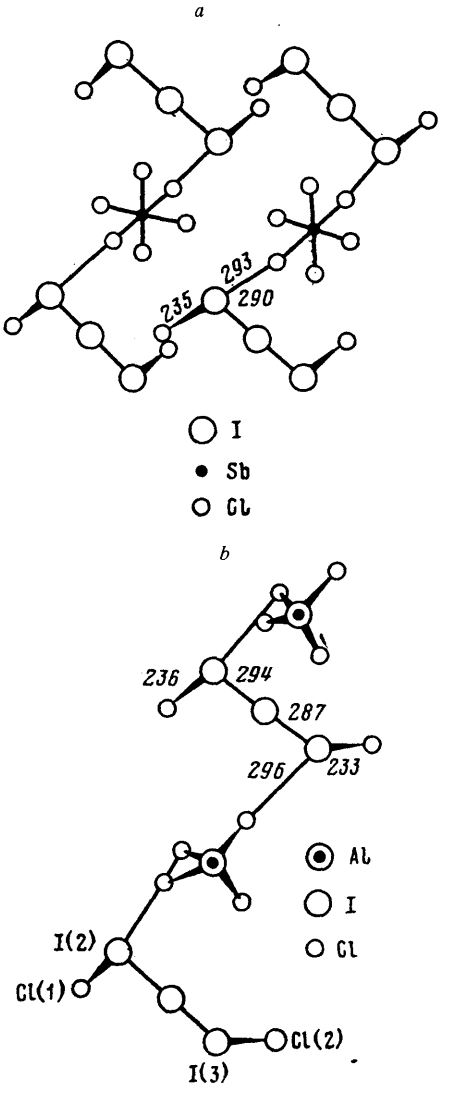


Figure 4. Fragments of the structures of $[I(ICl)_2][SbCl_6]$ (*a*) and $[I(ICl)_2][AlCl_4]$ (*b*)[48] (the interatomic distances are given in pm).

The effective charges on Cl(VII) and Br(VII) in the cations $[ClF_6]^+$ and $[BrF_6]^+$ are respectively +2.998 and +2.859, while those on the ligands are −0.332 and −0.310.[23–25] Most of the halogen cations investigated form crystals belonging to the triclinic and monoclinic systems (Table 1). Almost all the anions, except $[AlCl_4]^-$ and $[BF_4]^-$, have a somewhat distorted octahedral symmetry, ranging from O_h to D_{4h}, owing to the presence of bridging ligands.[17] The octahedral structure of the cations and anions increases the symmetry of the crystal lattice of the halogen cations to the symmetry corresponding to the cubic system (space group P_a3). In particular, $[IF_6][AuF_6]$, $[IF_6][SbF_6]$, $[IF_6][AsF_6]$, $[BrF_6][AsF_6]$, and $[ClF_6][PtF_6]$ crystallise in the cubic system with the parameter *a* equal to respectively (pm) 957.3,[8,65] 606.9,[8,66] 949.3,[56,65] 939.4,[8,67] and 939.[68] Only the crystal lattice of $[IF_6][RuF_6]$ has different parameters (space group $P2_1/n$; $a = 981$, $b = 761$, and $c = 580$ pm; $\beta = 107.8°$).[65]

Table 1. Crystallographic characteristics of certain halogen cation compounds.

Compounds	Crystal system*	Space group	Crystal lattice parameters				Refs.
			a, pm	*b*, pm	*c*, pm	angles, °	
$[I_3][AsF_6]$	Tr	$P\bar{1}$	805.4	594.0	1050.3	103.1 (α); 88.9 (β); 100.3 (γ)	[15]
$[I_5][SbF_6]$	Tr	$P\bar{1}$	829	1561	839	81.5 (α); 110.0 (β); 85.5 (γ)	[37]
$[ClF_2][SbF_6]$	Tr	$P\bar{1}$	560	1055	530	92.1 (α); 91.8 (β); 91.5 (γ)	[16]
$[ClF_2][AsF_6]$	M	$A2/_a$	1067.6	767.3	806.4	113.4 (β)	[26]
$[BrF_2][SbF_6]$	Or	P_{cca}	1012	581	1095	—	[17, 18]
$[BrF_2][NbF_6]$	Or	P_{cca}	1006	596	1070	—	[47]
$[BrF_2]_2[GeF_6]$	M	$P2_{1/c}$	507	1382	645	116.6 (β)	[27, 63]
$[ICl_2][SbCl_6]$	T	$P4_1$	698	698	2420	—	[19]
$[ICl_2][AlCl_4]$	M	$P2_1$	692	1102	611	99.1 (β)	[19]
$[ICl_2][SbF_6]$	Or	C_{mca}	1075.1	1208.7	1298.2	—	[42]
$[I(ICl)_2][SbCl_6]$	Tr	$P\bar{1}$	709	1159	713	122.3 (α); 98.0 (β); 115.9 (γ)	[46–48]
$[I(ICl)][AlCl_4]$	M	$C2/_c$	2753	712	1419	110.4 (β)	[48]
$[IBr_2][Sb_2F_{11}]$	Or	P_{bca}	1444.5	1403.4	1272.5	—	[41]
$[I(IBr)_2][SbCl_6]$	Tr	$P\bar{1}$	713	722	775	88 (α); 83 (β); 81 (γ)	[48]
$[I(BrCl)][SbCl_6]$	Tr	$P\bar{1}$	708.4	629.9	1351.1	94.5 (α); 100.3 (β); 92.6 (γ)	[41]
$[BrF_4][Sb_2F_{11}]$	M	—	1419	1450	527	90.6 (β)	[52]
$[IF_4][SbF_6]$	T	$P4/_{nmn}$	589.2	—	1025.5	—	[64]
$[IF_4][Sb_2F_{11}]$	M	$P2/_{1/c}$	852	1482	998	112.7 (β)	[51]

*Abbreviations for crystal systems: Tr = triclinic, M = monoclinic, Or = orthorhombic, and T = tetragonal.

It is noteworthy that the cation $[BrF_2]^+$ forms with many singly charged anions crystals having almost identical crystal lattices (Table 1). The crystal lattices of $[I(IBr_2)][SbCl_6]$ and $[I(BrCl)][SbCl_6]$ are also very similar despite the different nature of the ligands in the cations. The replacement of the ligands in the anions for the same cation alters sharply the crystal system—cf $[ICl_2][SbCl_6]$ and $[ICl_2][SbF_6]$ in Table 1.

The crystal lattices of the halogen cation compounds consist of infinite chains of cations and anions linked by halide bridges. The compounds are therefore regarded as partly covalent *cis*-bridged polymers.[42] The most important optical constants of the crystals of the halogen cation compounds are still to be determined, but one can already say that the vast majority of the crystals must be optically anisotropic and biaxial.

III. THE ELECTRONIC, VIBRATIONAL, NQR, and NMR SPECTRA

The electronic spectra (Table 2) are mainly used for the identification of the cations from the values of ε, the wavelengths of the absorption band maxima, and the shape of the latter. The bathochromic and hypsochromic effects and the presence of isosbestic points, which might yield information about the number of different cations in solution, have not been investigated. It follows from Table 2 that, for a number of halogen cation compounds, the absorption band in the range 435–470 nm apparently corresponds to the $\Pi^0 \rightarrow \Pi^*$ transitions which should have a low value of ε ($\lg \varepsilon < 3.30$).

Table 2. Electronic spectra of halogen cation compounds in various solvents (298 K).

Cation	HSO_3F		HSO_3CF_3		H_2SO_4 (96%)		Refs.
	λ, nm	lg ε	λ, nm	lg ε	λ, nm	lg ε	
$[Br_3]^+$	292–300	—	—	—	—	—	[4,69–72]
	375–380*	—	—		—		
$[I_3]^+$	300–305	3.7	295	3.8	290	3.8	[7, 30, 36, 73–78]
	470–472	3.2	462	3.4	459	3.3	
$[I(IBr)]^+$	260	3.6	260*	3.7	255–270*	3.8	[77, 78]
	300*	3.3	300*	3.4	300*	3.4	
	414–420	2.9	418	3.0	408–490	3.1	
$[IBr_2]^+$	232	3.7	260	3.1	260	3.2	[8, 77–79]
	361	2.7	360	2.8	355	2.8	
	455*	~2.2	453*	2.3	540–535	—	
$[I(ICl)]^+$	230	—	235	—	—	—	[30, 46, 77, 78, 80]
	300	3.1	315	3.1	295–300	3.3	
	461	2.7	450	2.8	435	2.9	
$[ICl_2]^+$	275*	2.7	310	2.2	318	2.1	[8, 76–79]
	395	1.8	374	1.8	355*	1.9	
	486	1.7	471	1.7	448	1.7	

*There is a low-slope shoulder on the absorption curve.

The electronic spectra of solutions of certain halogen cation compounds have been little investigated. The cation $[I_5]^+$ in solution in HSO_3F is characterised by absorption bands at 240, 270, 345, and 450 nm, while in solution in 96% H_2SO_4 it is characterised by bands at 330 and 450 nm.[8] Absorption bands at 270 nm ($\lg \varepsilon = 3.0$), 340 nm ($\lg \varepsilon = 2.5$), and 488 nm ($\lg \varepsilon = 1.9$) correspond to the cation $[I(BrCl)]^+$ in solution in 96% H_2SO_4.[77,78] The reddish-brown colour of the solution and the appearance of absorption bands at 305 and 470 nm are characteristic of the cation $[I_3]^+$. The absorption band at 440 nm (solution in SO_2 [46]) corresponds to the cation $[I(ICl)_2]^+$, while the bands at 248–252 and 305 nm (solution in SbF_5) correspond to the cations $[BrCl_2]^+$ and $[Br(BrCl)]^+$.[72]

The main information about the vibrational spectra of polycrystalline halogen cation compounds are presented in Tables 3–5. They have been fairly completely analysed by Shamir.[8] It is noteworthy that the assignment of many bands is still obscure. According to Gillespie and Morton[4] and Surles and Quarterman,[88] the band at 384–387 cm^{-1} in the Raman spectrum of the cation $[ClF_2]^+$ corresponds to ν_2 vibrations, while according to Christe and co-workers[39,89] the band at 544 cm^{-1} corresponds to these vibrations. The same discrepancy has been observed also in the assignment of the 537 cm^{-1} band in the IR spectrum of the same cation. The identification of the bands in the vibrational spectra of the cations $[IBr_2]^+$ and $[ICl_2]^+$ is also uncertain.

The angular structure of the triatomic cations has been confirmed not only by the activity of the three normal vibrations ($2A_1 + B_1$) in the IR and Raman spectra but also by the similarity of the ν_1 and ν_3 frequencies. Furthermore, the virtual identity (to within ±10 cm^{-1}) of the vibration frequencies of the halogen cation compounds dissolved in HF and of the crystals of their compounds indicates the presence in the liquid and solid phases of the same discrete ions $[Hal(Hal')_2]^+$.

The frequencies of all nine species of the normal vibrations of the cations $[Hal(Hal')_4]^+$ ($4A_1 + A_2 + 2B_1 + 2B_2$) have been found in the Raman and IR spectra (Table 4). The most intense band in the range 720–820 cm^{-1} corresponds to the symmetrical (ν_1) and antisymmetric (ν_8) equatorial vibrations of the Hal–Hal' bond. The frequencies of the antisymmetric (ν_6, B_1) axial vibrations are apparently identical with the frequencies of the type ν_1 vibrations.

Table 5 shows that $\nu_1 < \nu_2$ for the cations $[BrF_6]^+$ and $[IF_6]^+$, in contrast to $[ClF_6]^+$. This has also been confirmed by quantum-mechanical calculations.[104] In the octahedral ions with heavy complex-forming agents, the fully symmetrical vibration leads to the appearance of polarised lines in

Table 3. Vibrational spectra of triatomic halogen cations.

Cation	Type of spectrum	Frequency, cm^{-1}			Refs.	Cation	Type of spectrum	Frequency, cm^{-1}			Refs.
		ν_1	ν_2	ν_3				ν_1	ν_2	ν_3	
$[Cl(ClF)]^+$	IR	530	290	590	[4, 5, 28, 50, 70]	$[Br_3]^+$	IR	—	—	—	[8, 69, 70]
$[Cl(ClF)]^+$	R	744	535–540	293–299		$[Br_3]^+$	R	290	140	288	
$[ICl_2]^+$	IR	368–370	—	—	[70, 77, 78, 80–83]	$[BrF_2]^+$	IR	705–713	308	695	[5, 44, 70, 87, 88, 92–94]
$[ICl_2]^+$	R	366–371	143–149	350–364		$[BrF_2]^+$	R	704	362	702	
$[I(ICl)]^+$	IR	—	—	—	[46, 70, 77, 84]	$[I_3]^+$	IR	207	114	233	[8, 70]
$[I(ICl)]^+$	R	354–359	124–126	184		$[I_3]^+$	R	207	114	233	
$[Cl_3]^+$	IR	490	225	508	[4, 28, 70, 77, 85]	$[IBr_2]^+$	IR	248	—	258	[41, 77, 78, 82]
$[Cl_3]^+$	R	490	225	508		$[IBr_2]^+$	R	232	123–127	257	
$[ClF_2]^+$	IR	789–805	381–387	815	[5, 39, 44, 70, 86–91]	$[I(BrCl)]^+$	IR	—	—	—	[41, 77, 80, 84]
$[ClF_2]^+$	R	809–811	384	808–830		$[I(BrCl)]^+$	R	242 (I–Br); 362 (I–Cl)	129	250 (I–Br); 356 (I–Cl)	

R = Raman spectrum (Editor of Translation).

the Raman spectrum (ν_1), while lower symmetry vibrations give rise to depolarised scattered radiation (ν_2) and causes the reversal of the frequencies ν_1 and ν_2.[104]

The vibrational spectrum of the cation $[ClF_6]^+$ resembles the spectrum of the isoelectronic SF_6 molecule and the isotopic splitting ($^{35}Cl-^{37}Cl$) of the ν_3 band (890 cm^{-1}), amounting to 13 cm^{-1}, agrees well with the calculated value (12.5 cm^{-1}) for the octahedral structure.[99] In the Raman spectrum of the cation $[ClF_6]^+$, the weak band at 706 cm^{-1}, identified[62] as the $2\nu_6(A_{1g} + E_g + F_{1g} + F_{2g})$ band, is involved in Fermi resonance with the $\nu_1(A_{1g})$ band at 688 cm^{-1} (Table 5).

For the series of cations $[ClF_6]^+$, $[BrF_6]^+$, and $[IF_6]^+$, the stretching force constants f_r are respectively 4.98, 4.90, and 5.42 mdyn A^{-1}.[67] These values are highest for the Cl–F, Br–F, and I–F bonds owing to the high oxidation states of the complex-forming agent.

Extensive investigations of the NQR spectra of the ligand and central atom nuclei established the non-equivalence of the halogen atoms in the cations and the presence of bridge bonds between the cation and anion.[8,105] In particular, analysis of the ^{127}I NQR spectrum of the compound $[I_3][AlCl_4]$ confirmed that one of the iodine atoms in the cation is the complex-forming agent,[30,31] and the cation $[I_3]^+$ should therefore be described by the formula $[I(I)_2]^+$. Furthermore, the dimorphism of $[I_3][AlCl_4]$ has been observed. The frequency 400 ± 5 MHz in the ^{127}I NQR spectrum characterises the complex forming agent in the cation $[I_5]^+ = [I(I_2)_2]^+$.[30]

The frequency of the ^{35}Cl signal in the NQR spectra (at −195 °C) of the halogen cations $[ClF_2]^+$ and $[ClF_4]^+$ is determined, according to the authors,[106,107] by the electron-accepting capacity of the anion. The signal is more intense, the higher the electron-accepting capacity of the anions, which can be arranged in the following sequence in terms of the increase of this capacity: $[TaF_6]^- < [NbF_6]^- < [SbF_6]^- < [AsF_6]^- < [Sb_2F_{11}]^-$. The asymmetry parameter η of the electric field gradient of the complex forming atoms of the cations $[ClF_4]^+$ and $[IF_4]^+$ is 48–50%.[108] After the appearance in the halogen cations of the *cis*-configuration of the Cl–F and I–F bridge bonds with the two SbF_6 octahedra of the $[Sb_2F_{11}]^-$ anions, the values of η and the quadrupole interaction constants diminish somewhat.[108]

Many halogen cation compounds have been investigated by NMR. Two equally intense signals (δ = −256 and −274 p.p.m.), measured relative to $CFCl_3$ at a temperature below −60 °C, in the ^{19}F NMR spectrum of the cation $[ClF_4]^+$ indicate the non-equivalence of the positions of the two fluorine atoms.[53,109,110] which corresponds to a trigonal-bipyramidal structure of the cation and the presence of bridging F atoms. Analysis of the ^{35}Cl and ^{127}I NMR spectra of the cation $[I(ICl)]^+$ established[30,31] that one of the iodine atoms is the complex-forming agent, while the other is the ligand. The angular structure of the cations $[ClF_2]^+$ and $[BrF_2]^+$ [109–112] and the octahedral structure of the cations $[ClF_6]^+$ and $[BrF_6]^+$ [61,99,109,113] have been confirmed.

The ^{129}I Mössbauer spectrum of the cation $[IF_6]^+$ consists of a single signal with the isomeric shift $\delta = -4.68$ mm s^{-1}, which is characteristic of highly symmetrical cations.[8,59]

IV. THERMODYNAMICS OF FORMATION AND DECOMPOSITION

The appearance in solution of the cations $[Hal(Hal')_n]^+$ is not associated with the usual complex-forming reactions and the problem of consecutive equilibria. However, such cations are complex species and enter the ligand substitution, addition, and redistribution reactions characteristic of complex compounds. For example, the following reactions take place in solution in HSO_3F:[77,78]

$$[IBr_2]^+ + Cl_2 \rightleftharpoons [ICl_2]^+ + Br_2;\ [IBr_2]^+ + [ICl_2]^+ \rightleftharpoons 2[I(BrCl)]^+;$$
$$[I(I)_2]^+ + [ICl_2]^+ \rightleftharpoons 2[I(ICl)]^+;\ I(SO_3F) + IBr \rightleftharpoons [I(IBr)](SO_3F).$$

Table 4. Vibrational spectra of penta-atomic halogen cations.

Cation	Type of spectrum	Frequency (cm^{-1}) and band assignment								Refs.
		$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(A_1)$	$\nu_5(A_2)$	$\nu_7(B_1)$	$\nu_8(B_2)$	$\nu_9(B_2)$	
$[ClF_4]^+$ $[ClF_4]^+$	IR R	799–802 796–803	568 568	515–519 511	236 —	474 —	536 536	822–830 826	— 395	[53, 86, 95, 96]
$[BrF_4]^+$ $[BrF_4]^+$	IR R	— 724	606 604	— 383	— 214–219	690* 703*	419 416–424	730 736	369 365–371	[61, 78, 95, 97]
$IF_4]^+$ $IF_4]^+$	IR R	728 729–732	— 614–621	345 342	— 241	— 655*	388 385–434	719 720	311 316	[53, 94, 98]

*The data refer to the $\nu_6(B_1)$ vibrations.

Table 5. Vibrational spectra of hepta-atomic halogen cations.

Cation	Type of spectrum	Frequency (cm^{-1}) and band assignments						Refs
		$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	$\nu_5(F_{2g})$	$\nu_6(F_{2u})$	
$[ClF_6]^+$ $[ClF_6]^+$	IR R	— 679–689	— 580–630	890 —	540–590 —	— 515	— 706 ($2\nu_6$)	[61, 62, 68, 86, 95, 99, 100]
$[BrF_6]^+$ $[BrF_6]^+$	IR R	— 658	— 668	775 —	430 —	— 405	— —	[60, 61, 67, 101]
$[IF_6]^+$ $[IF_6]^+$	IR R	— 708	— 732	793 —	343 —	— 340	250 —	[4, 56, 57, 65, 66, 102, 103]

When the anion is replaced, some of these reactions become impossible under previous conditions. In particular, the reaction

$$I(SO_3CF_3)+Hal_2 \rightleftarrows [I(Hal)_2](SO_3CF_3)$$

takes place only with participation of $Hal_2 = Br_2$; this is due to the low solubility of $I(SO_3CF_3)$ and its polymeric structure.[77,78]

In the reactions presented above, the more electropositive ligand is always substituted by a more electronegative one and the less electropositive complex-forming agent is replaced by a more electropositive one. Reactions are known[114] in which two ligands are substituted at once:

$$[Cl(ClF)][AsF_6]+Cl_2 \rightleftarrows [Cl(Cl)_2][AsF_6]+ClF\ ;$$
$$[Cl(ClF)][AsF_6]+SOF_2 \rightleftarrows [Cl(SOF_2)][AsF_6]+ClF\ .$$

The latter reaction occurs even at −130 °C with 85% yield. The substitution of two ligands is apparently preceded by an elimination reaction with formation of two radical species, Cl· and F·, which then combine to form the molecule ClF.

The substitution reactions make it possible to establish the following stability series of the cations:[115,116]

$$[IF_2]^+ > [BrF_2]^+ > [ClF_2]^+;\ [ICl_2]^+ > [BrCl_2]^+ > [Cl(Cl)_2]^+.$$

The mechanism of the formation of halogen cation compounds has not been ultimately elucidated. It has been suggested that[6,8,9,117] interhalogen compounds or halogens initially dissociate:

$$2BrF_3 \rightleftarrows [BrF_2]^+ + [BrF_4]^-;\ 3IBr \rightleftarrows [I(IBr)]^+ + [IBr_2]^-;$$
$$4ICl \rightleftarrows [I(ICl)_2]^+ + [ICl_2]^-;\ 3I_2 \rightleftarrows [I_3]^+ + [I_5]^-\ \text{etc.},$$

According to the data of Surles and Hyman,[93,118] on dissociation of BrF_3 (at 30 °C), the concentration of the ions formed is 0.9 ± 0.1 M. The equilibrium constant for the reaction

$$BrF_3 + ClF_3 \rightleftarrows [ClF_2]^+ + [BrF_4]^-$$

at 25 °C and for a BrF_3 mole fraction of 0.22–0.85 is 1×10^{-4}.[118,119] The introduction of electrophiles and nucleophiles (AsF_5, $SbCl_5$, $AlCl_3$, etc.) shifts the equilibrium towards the formation of halogen cation compounds:

$$[BrF_4]^- + SbF_5 \rightleftarrows BrF_3 + [SbF_6]^-;\ [ICl_2]^- + AlCl_3 \rightleftarrows ICl + [AlCl_4]^-\ \text{etc.},$$

In the intermediate stages of the formation of the cations, there is a possibility of the appearance of radical-anions. For example, it has been assumed[120] that the abstraction of electrons from Cl_2 can induce the formation of the planar radical cation Cl_4^+ from Cl_2^+ and Cl_2 (weak $\pi-\pi^*$ interaction).

In our view, another mechanism for the formation of halogen cation compounds is also possible:

$$BrF_3 + SbF_5 \rightleftarrows BrF_3 \cdot SbF_5 \rightleftarrows [BrF_2][SbF_6]\ .$$

According to this scheme, an adduct without a rigid nuclear configuration is formed initially and then bridge bonds arise between BrF_3 and SbF_5 as a result of the migration of the nuclei and the redistribution of electron density by virtue of the low activation energy. After this, the fluoride ion is transferred.

The calorimetric method has not so far come to be widely used in the study of the formation reactions of halogen cation compounds. Systematic investigations in this field are only just beginning. In particular, the enthalpies of solution (at 25 °C) of SbF_5, SnF_4, and TaF_5 in BrF_3, which represent the overall energies of the dissolution process and the chemical reaction, are respectively −92.3 ± 0.3, −58.8 ± 0.7, and −45.2 ± 0.8 kJ per mole of the dissolved fluoride.[119] On the other hand, the enthalpies of formation ($-\Delta H^0_{298}$) of $[BrF_2][SbF_6]$, $[BrF_2]_2[SnF_6]$, and $[BrF_2][TaF_6]$ are respectively 1773, 1505, and 2251 kJ mol^{-1}. The last quantity includes ΔH^0_{298} for the formation of BrF_3 and TaF_5. On the other hand, the enthalpies of solution of the same halogen cation compounds in BrF_3 at 25 °C are respectively −4.94, −2.00, and −1.40 kJ mol^{-1}.[119] For the reaction

$$K[BrF_4]+[BrF_2][SbF_6]=K[SbF_6]+2BrF_3\ ,$$

in BrF_3, $\Delta H^0_{298} = -19.1 \pm 1.0$ kJ mol^{-1}. With increase of the degree of solvolysis of the interacting substances, this quantity diminishes and amounts to −15.3 ± 0.8 kJ mol^{-1} for the same reaction involving $[BrF_2][TaF_6]$.[119]

The thermal stabilities of the halogen cation compounds are different. Whereas the compounds containing the cation $[Cl_3]^+$ decompose fully at 25 °C, $[Br_3][AsF_6]$ dissociates only above 70 °C with evolution of Br_2, while in an atmosphere of nitrogen it sublimes without decomposition at 30–50 °C.[71] The halogen cation compounds $[I_3][AlCl_4]$ and $[I_3](SO_3F)$ melt congruently at 45° ± 1 °C[30,31] and at 92–101 °C[38,74] respectively.

Table 6 presents certain thermodynamic characteristics of the thermal decomposition reactions.

$$[Hal(Hal')_n][MHal_m'] \rightleftarrows Hal(Hal')_{n+1} + MHal'_{m-1}\ .$$

The enthalpies of the thermal dissociation reactions ΔH^0_g, listed in Table 6, were found from the slopes of the $\lg p = f(1/T)$ curves subject to the condition that the enthalpies of sublimation of the test substances are zero.

Table 6. Certain thermodynamic characteristics of the thermal dissociation of halogen cation compounds.

Substance	lg p (mmHg)	T, K	ΔH^0_g, kJ mol^{-1}	$-\Delta H^0_{298}$, kJ mol^{-1}	Refs.
$[ClF_2][BF_4]$	$\frac{-2576+16}{T}+(12.00\pm0.05)$	243–293	98.7	1394.5	[14, 89, 121]
$[ClF_2][PF_6]$	$-1798/T+10.53$	—	68.6	1827.1	[8, 14, 89]
$[Cl(ClF)][AsF_6]$	$-2391.6/T+11.71$	209–255	137.2	1487	[50]
$[BrF_2][SbF_6]$	$-3030/T+7.66$	498–623	116.3	1773*	[12, 119, 122]
$[ClF_4][AsF_6]$	$-2763.6/T+12.2$	242–283	105.6	1576.5	[123]
$[IF_6][AsF_6]$	$-4800/T+16.42$	—	183.7	2251	[56]

Notation: p is the thermal dissociation pressure and ΔH^0_g the enthalpy of thermal dissociation.
*Found from calorimetric measurements.[119]

The complex $[ClF_2][BF_4]$ dissociates fully into ClF_3 and BF_3 in the gas phase at temperatures above 30 °C, while $[Cl(ClF)][BF_4]$ decomposes already at temperatures above −112 °C and in the liquid state this substance is unknown.[50] The products of the thermal decomposition of the complex $[Cl(ClF)][AsF_6]$ are gaseous ClF and AsF_5. $\Delta G^0_T = 9.0$ kJ mol^{-1} and $\Delta S^0_T = 491.2$ J mol^{-1} K^{-1} for this reaction.[50] The enthalpy of the thermal dissociation of $[BrF_2][SbF_6]$ in the range 130–350 °C, calculated from vapour pressure data, is 116.3 kJ mol^{-1}, while the calorimetric value is 186 kJ mol^{-1}.[119] The thermal dissociation pressure of $[BrF_2][BF_4]$ at −31 °C is 4 mmHg, while at 23 °C the halogen cation compound decomposes fully.[124]

The stability of the complexes with the cation $[IF_2^+]$ increases in the series of anions $[BF_4]^- < [AsF_6]^- < [SbF_6]^-$. Whereas the compound $[IF_2][BF_4]$ is stable only in solution of acetonitrile, the compound $[IF_2][SbF_6]$ withstands heating to 45 °C.[125,126] $\Delta G^0_T = 2.9$ kJ mol^{-1} and $\Delta S^0_T = 344.3$ J mol^{-1} K^{-1} have been found[123] for the reaction

$$[ClF_4][AsF_6]\,(cryst.) = ClF_5(gas) + AsF_5(gas)$$

The products of the dissociation of $[ClF_4][PtF_6]$ above 25 °C (the vapour pressure at 23 °C is 2 mmHg) are ClF_5, PtF_4, and PtF_6.[91]

The thermal decomposition of substances containing the cation $[ClF_6]^+$ is accompanied by the evolution of fluorine.[62,100] The complex $[ClF_6][PtF_6]$ dissociates above 140–180 °C,[68] while $[IF_6][AsF_6]$ sublimes at 120–140 °C with decomposition into IF_7 and AsF_5 (ΔG_T^0 = 32.6 kJ mol^{-1} and ΔS_T^0 = 506.3 J mol^{-1} K^{-1}).[56,127]

Among the known compounds of the hexafluoride (VII), the complex $[IF_6][BF_4]$ is the least stable, the vapour pressure amounting to 10 mmHg at −60 °C.[127]

V. SYNTHESIS OF HALOGEN CATION COMPOUNDS

The methods of synthesis of halogen cation compounds are based mainly on reactions between interhalogen compounds and halogens and the halides of Group IIIA–VA elements in their highest oxidation states. The halogen cation compounds obtained by one or other preparative method but having the same compositions can exhibit appreciably different melting points[8] and other physical characteristics, which is due to the presence of admixtures of the initial reactants and side products of the reaction. The degree of contamination is reduced only after carrying out the synthesis within the limits of the region of crystallisation of the target products, determined from the phase diagrams of the corresponding systems.

The cation $[Cl(Cl)_2]^+$. The appearance of a phase containing $[Cl_3]^+$ has been observed in the systems Cl_2–ClF–AsF_5 (SbF_5, $SbCl_5$, HF) at −76 °C and below,[4,7,28,70] in the system $[Cl(ClF)][AsF_6]$–Cl_2 at −78 °C,[28] and in the system Cl_2–$SbCl_3$ at −51 °C.[128] The formation of the cation $[Cl_3]^+$ has not been observed in the systems HSO_3F–SO_3–Cl_2–$SbCl_5$ (25 °C, 3 atm)[85] and ClF–Cl_2–BF_3 (at temperatures from 130° to 25 °C).[4,7]

The cation $[Br(Br)_2]^+$. When BrF_5 and Br_2 are condensed in a quartz reactor containing a 30% excess of AsF_5(SbF_5) at −196 °C, brown crystals are formed[71] via the reaction

$$7Br_2+BrF_5+5AsF_5=5[Br_3][AsF_6]\ .$$

The reaction,[71,129]

$$2O_2[AsF_6]+3Br_2=2[Br_3][AsF_6]+2O_2\ .$$

leads to the same result. In order to avoid the formation of the cation $[Br_2]^+$, the molar ratio Br_2/BrF_5 in the first reaction should not exceed 4.5.[72]

The appearance of the cation $[Br_3]^+$, noticed in a number of investigations[4,7,29,70,130,131] in the systems Br_2–$S_2O_6F_2$ (SbF_5, HSO_3F, SO_3) is caused by reactions of the type

$$3Br_2+S_2O_6F_2\rightleftarrows 2[Br_3]^++2SO_3F^-\ .$$

The cations $[I(I)_2]^+$ and $[I(I_2)_2]^+$. The formation of new phases with the cations $[I_3]^+$, $[I_5]^+$, and $[I_7]^+$ has been postulated in the systems I_2–$S_2O_6F_2$[38] and I_2–ICl–$AlCl_3$.[30,31] These phases could not be isolated from the melt. Spectroscopic analysis (^{19}F NMR, IR) of the liquid phases failed to confirm the formation of the cations $[I_3]^+$ and $[I_7]^+$ in the first system. The results of cryoscopic measurements for the same system are contradictory and do not lead to unambiguous conclusions.[38,75,132]

The black-brown powder of $[I_3](SO_3F)$ was obtained[74] only after prolonged treatment of an excess of I_2 with pure $S_2O_6F_2$ at 20 °C with subsequent heating of the mixture to 85 °C and cooling to −180 °C. The possibility of the synthesis of the complex has been pointed out in several investigations.[4,36,133] At a low temperature the interaction of I_2 and $S_2O_6F_2$ leads to formation of the diamagnetic cation $[I_4]^{2+}$ together with $[I_3]^+$,[4,35,36,134] while according to a number of other data[7,29,75] the cation $[I_5]^+$ is also formed.

The compounds $[I_3][AsF_6]$,[15,135] $[I_5][SbF_6]$,[37] and $[I_7]$.$[SO_3F)_2$[38] have been obtained in a crystalline state by purely preparative methods. The composition of the last phase requires confirmation.

The results of the study of the systems I_2–HIO_3 (KI, ICl, I_2O_5)–H_2SO_4($HSClO_3$, $K_2S_2O_8$) by conductimetric titration methods, the reddish-brown colour of the solutions, and the electronic spectra indicate the formation of the cation $[I_3]^+$.[1,73,76,133,136] It has been suggested that the cation $[I_3]^+$ should also be formed in the systems I_2–$H_2S_2O_7$,[137] I_2–HSO_3F,[138] I_2–SO_2–SbF_5,[70] ICl–H_2SO_4, I_2–HCl–BCl_3–$K_2S_2O_8$, I_2–CF_3COOH–BF_3–$K_2S_2O_8$, and ICl–BF_3–CF_3COOH.[136] The cation $[I_5]^+$ has been detected in the systems I_2–HIO_3–H_2SO_4 with a molar ratio $I_2/HIO_3 > 7$,[73,133] and also in the systems I_2–H_2SO_4–SO_3[139] and I_2–SbF_5–AsF_3.[37,140]

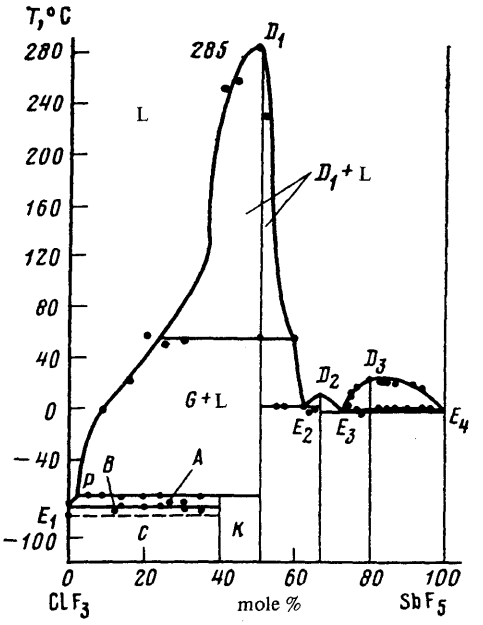


Figure 5. Phase diagram for the system ClF_3–SbF_5:[141] D_1 = α-$[ClF_2][SbF_6]$; D_2 = $ClF_3.2SbF_5$; D_3 = $ClF_3.4SbF_5$; G = β-$[ClF_2][SbF_6]$; P = $3ClF_3.2SbF_5$; A = $3ClF_3.2SbF_5$ + L; B = $3ClF_3.2SbF_5$ + α-ClF_3; C = $3ClF_3.2SbF_5$ + β-ClF_3; L = liquid phase; K = $3ClF_3.2SbF_5$ + β-$[ClF_2][SbF_6]$.

The cation $(ClF_2)^+$. A thorough study[141] of the system ClF_3–SbF_5 (Fig.5) showed that the interaction of its components can result in the formation of not only $[ClF_2][SbF_6]$ and $[ClF_2][Sb_2F_{11}]$ but also of two new phases: $3ClF_3.2SbF_5$ (P) and $ClF_3.4SbF_5$ (D_3). The coordinates of the eutectic points are E_1 = 98 mol % ClF_3, m.p. −72 °C; E_2 = 37.95 mol %, 2 °C; E_3 = 27.50 mol %, 0 °C; E_4 = 1.2 mol %, +7 °C. The compound $[ClF_2][SbF_6]$ is dimorphic with a phase transition temperature of 55 °C. The congruent

melting points of the phases D_2 and D_3 are respectively 11° and 25 °C.

Compounds with the cation $[ClF_2]^+$ are synthesised either by condensing ClF_3 on AsF_5 {SbF_5, BF_3, PtF_6, $O_2[PtF_6]$} at −196 °C with subsequent removal of the excess ClF_3 in a stream of nitrogen or by the direct reaction of ClF_3 with AsF_3 (SbF_3, BF_3), which proceeds vigorously even at −70 °C. The excess ClF_3 can convert the chlorides or fluorides of the elements in the lowest oxidation state initially into Lewis acids and then into compounds with the cation $[ClF_2]^+$.[127,142] The compounds $[ClF_2][SbF_6]$,[16] $[ClF_2][AsF_6]$,[26,89,127,143] $[ClF_2][BF_6]$,[12,14,89,121] and $[ClF_2][PtF_6]$[90,144–146] were obtained in this way in the crystalline state. The individuality of some of these compounds is open to doubt, in particular the melting point data[127,142] for $[ClF_2][SbF_6]$ (75–78 °C) differ by 207–210 °C from those in another study[141] (Fig. 5).

The synthesis of $[ClF_2][IrF_6]$ and $[ClF_2][PF_6]$ has been reported.[12,26] The system ClF_5–HF is of the eutectic type (44% ClF_3, m.p. −110.7 °C),[9,12,88,147] although the cations $[ClF_2]^+$ have also been detected in solution.[88,148] The components of the ClF_3–UF_6 system do not interact either.[9,149]

The cation $[Cl(ClF)]^+$. Using the synthetic methods described above, the compound $[Cl(ClF)][AsF_6]$, which is stable below −70 °C, was obtained.[50] In solution in the HF–SbF_5 mixture, the cation decomposes even at −76 °C.[4,28]

The cation $[BrF_2]^+$. The formation of not only $[BrF_2]$.$[SbF_6]$ (m.p. 129 °C) but also of a series of other new phases, namely $BrF_3.3SbF_5$ (m.p. 33.5 °C), $3BrF_3.2SbF_5$, and $3BrF_3.SbF_5$ has been established in the system BrF_3–SbF_5 (Fig. 6). The incongruent melting points of the last two phases are respectively 30.8° and −16.3 °C.[150]

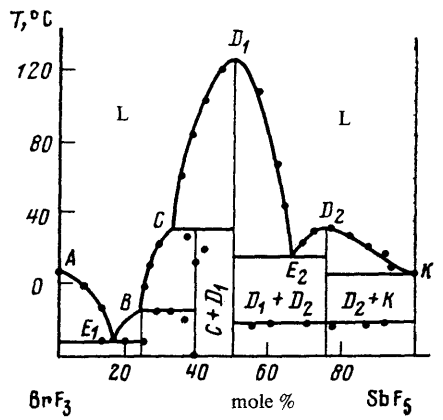


Figure 6. Phase diagram for the system BrF_3–SbF_5;[150] $D_1 = [BrF_2][SbF_6]$; $D_2 = BrF_3.3SbF_5$; $A = BrF_3$; $B = 3BrF_3.SbF_5$; $C = 3BrF_3.2SbF_5$; $K = SbF_5$. Coordinates of the eutectic points: E_1 = 83.0 mole % BrF_3, m.p. 33.1 °C; E_2 = 33.5 mole % BrF_3, m.p. 15 °C.

The formation of the compound $[BrF_2]_2[SnF_6]$, melting incongruently at 93° ± 1 °C, has been observed[151] in the system BrF_3–SnF_4, which has been only partly investigated owing to the high viscosity of the melt. The formation of two incongruently melting phases has been established in the BrF_3–PtF_4 system:[152] $[BrF_2]_2[PtF_6]$ and $7BrF_3.PtF_4$.

A whole series of compounds with the $[BrF_2]^+$ cations have been obtained, incorporating the following anions apart from those indicated above: $[AsF_6]^-$,[92] $[BF_4]^-$,[63,124,153] $[NbF_6]^-$, $[TaF_6]^-$, $[BiF_6]$,[17,154,155] $[GeF_6]^{2-}$,[27,63,92] $[PdF_4]^-$, $[RuF_6]^-$, $[AuF_4]^-$, and $[RhF_6]^-$.[154,156–159] The data concerning the synthesis[153] of $[BrF_2][BF_4]$, allegedly stable at room temperature, were not confirmed.[124] The interaction of BrF_3 and BF_3 affords the compounds $[BrF_2][BF_4]$ (stable below −80 °C) and $[BrF_2][B_2F_7]$ (stable below −120 °C).[63,124] The separation of these compounds without the preliminary study of the system BrF_3–BF_3 is very difficult.

The above halogen cation compounds are synthesised by the methods involving the direct interaction of the fluorides, chlorides, and oxides of the elements with an excess of BrF_3. The residual BrF_3 is then removed *in vacuo*.[92,160–162] The reaction with the oxides proceeds vigorously and is accompanied by the evolution of O_2, Br_2 being introduced into the reactor to slow it down.

The method involving the direct interaction of BrF_3 with powdered metals at temperatures ranging from 190 °C and above has also been recommended.[155,156,158,159,161,163] For platinum metals, a mixture of BrF_5 and Br_2 is used instead of BrF_3.[164] The reactions of BrF_3 with SO_3, $Br(SO_3F)_3$, and $F(SO_3F)$, and of BrF_5 with SO_3 result in the formation of the same compound $[BrF_2](SO_3F)$.[111,165]

The cations $[BrCl_2]^+$ and $[Br(BrCl)]^+$. They exist only in liquid phases of the systems Cl_2–$Br(SO_3F)$–SbF_5 and Cl–$Br_2(Sb_3F_{16})$.[72]

The cation $[IF_2]^+$. It is formed in the systems IF_3–BF_3–CH_3CN (at −45 °C) and $I(SO_3F)$–$S_2O_6F_2$.[12,74] The interaction of IF_3 with $AsF_5(SbF_5)$, cooled to −78 °C, results in the formation in the solid state of $[IF_2][AsF_6]$ (decomposes at −22 °C) and $[IF_2][SbF_6]$, which can withstand heating to 45 °C.[125,126]

The cation $[ICl_2]^+$. It forms red and orange-red crystals with the anion SO_3F^- when $I(SO_3F)$ is acted upon by liquid chlorine (at −70 °C) with subsequent increase of temperature to 20 °C[74,77,82] or when a suspension of I_2Cl_6 in CCl_4 (below −10 °C) is mixed with a limited amount of SO_3.[166,167] The compounds of dichloroiodine (III) have been obtained with the following anions: $[SbF_6]^-$—by adding I_2Cl_6 to a solution of SbF_5 in SO_2ClF with subsequent removal of the excess SO_2ClF by slow distillation;[42] $[Sb_2F_{11}]^-$—by the reaction of I_2Cl_6 with SbF_5;[78] $[SbCl_6]^-$—by the reaction of I_2Cl_6 with an excess of $SbCl_5$ at 100 °C[19,81,83,168] or on mixing I_2, $SbCl_5$, and an excess of liquid chlorine (at −196 °C) with subsequent raising of the temperature to −80 °C;[80,84,169] $[AlCl_4]^-$—by heating equimolar amounts of I_2Cl_6 and $AlCl_3$ in CCl_4 or $CHCl_3$[19,81,168,169] and also by the reaction of I_2Cl_6 with $AlCl_3$ in a sealed tube at 100 °C.[83]

The cation $[I(ICl)]^+$. It follows from the phase diagram for the system ICl–$AlCl_3$[30,170] that the reaction of ICl with $AlCl_3$ leads to the formation of the compound $2ICl.AlCl_3 = [I(ICl)][AlCl_4]$, melting incongruently at 53 °C, in which the ligands are the I^- and Cl^- ions. Signs of the appearance of an analogous compound have been observed[171,172] also in the system ICl–$AlCl_3$–$C_6H_5NO_2$. According to Pohl and Saak,[48] only the compound $[I(ICl)_2][AlCl_4]$ is formed in the reaction of ICl with $AlCl_3$. The reaction

$$I_2 + 2SbCl_5 \rightleftharpoons [I(ICl)][SbCl_6] + SbCl_3,$$

is apparently possible in the system I_2–$SbCl_5$.[140,173–176] The dark-brown crystals of $[I(ICl)][SbCl_6]$ have been obtained by the interaction of ICl and $SbCl_5$ and of I_2, $SbCl_5$, and

Cl_2 (at −196 °C).[47,70,80,84] It has been suggested[8,80] that the last reaction is followed by the side process

$$I_2+Cl_2\rightleftharpoons 2ICl$$

which initiates the reaction

$$ICl+Cl_2+SbCl_5=[ICl_2][SbCl_6]\ .$$

It is believed[8] that the nI_2 + ICl + $SbCl_5$ interaction (n = 1–3) always entails the formation of the cation $[I(ICl)]^+$ in the first stage regardless of the ratio of the initial components, pressure, and temperature.

The formation of two compounds, namely $[I(ICl)][SbCl_6]$ and $[I(ICl)_2][SbCl_6]$, melting congruently at almost the same temperature (62.5 °C), has been established in the system ICl–$SbCl_5$.[177] Whereas the compound $[I(ICl)].[GaCl_4]$, melting incongruently at 28.5 °C, is formed in the system ICl–GaCl,[173] the only product in the system ICl–$SbCl_3$ is the adduct $SbCl_3.5ICl$ [178] ($ICl.SbCl_3$ is formed according to other data[173,179]). No interaction has been observed between ICl and $AsCl_3$.[180] Similarly only the adduct $ICl.TaCl_5$, melting incongruently at approximately 102 °C, is formed in the system ICl–$TaCl_5$, while the system ICl–$NbCl_5$ is of the purely eutectic type.[181]

The reactions of $I(SO_3F)$ and ICl (at 50 °C) and of $[I_3].(SO_3F)$ and $[ICl_2](SO_2F)$ in a stream of dry nitrogen[77,78] lead to the formation of $[I(ICl)](SO_3F)$.

The cation $[I(ICl)_2]^+$. The mechanism of reactions in which the ICl molecules become the ligands while iodine acquires the +1 oxidation state has not been ultimately elucidated. Thus the reaction of ICl with $SbCl_5$ or $AlCl_3$ entails the formation, together with the cation $[I(ICl)]^+$, also of the cation $[I(ICl)_2]^+$.[48,174,182,183] According to other data,[46,47] the compound $[I(ICl)_2][SbCl_6]$ can also cyrstallise from a solution of I_2Cl_6 and $SbCl_3$ in SO_2.

The cation $[IBr_2]^+$. Compounds with this cation cannot be obtained by the direct interaction of Lewis acids (SbF_5, AsF_5, $AlCl_4$, etc.) with IBr_3 or I_2Br_6, since the latter have not so far been obtained. For this reason, $[IBr_2][Sb_2F_{11}]$ is synthesised in the following manner. A solution of SbF_5 in SO_2 is mixed initially with IBr until the appearance of a precipitate of SbF_5, which is filtered off and SO_2 is removed; the final product is extracted from the paste-like residue with SO_2ClF.[41] The same compound can be obtained in the exchange reaction of $[IBr_2](SO_3F)$ with a large excess of SbF_5 on heating to 70 °C.[78] Compounds with the anions SO_3F^- and $SO_3CF_3^-$ are formed on heating to 50 °C a mixture of $I(SO_3F)$ or $I(SO_3CF_3)$ with Br_2.[77,78,82]

The cation $[IBr_2]^+$ has been detected in the system I_2–Br_2–HIO_3–H_2SO_4 at 25 °C with the molar ratio I_2/HIO_3 = 2.0.

The formation of the cations $[IBr_2]^+$ has not been established in the systems IBr–$AlBr_3$,[184] IBr–$GaBr_3$,[173] IBr–$SbBr_3$,[178] and IBr–$AlBr_3(SbBr_3)$-$C_6H_5NO_2$.[182,185] The adduct $IBr.AlBr_3$ was isolated in the first system.

The cations $[I(IBr)]^+$ and $[I(IBr)_2]^+$. When $I(SO_3F)$ and IBr interact (at 50–75 °C), the compound $[I(IBr)](SO_3F)$, melting incongruently at 70 °C, crystallises,[77] while the almost black crystals of $[I(IBr)_2][SbCl_6]$ can be obtained by the reaction of ICl, IBr, and $SbCl_5$.[48] Both cations apparently exist in the same systems and their crystallisation regions are determined by the ratio of the components, as in the systems of the cations $[I(ICl)]^+$ and $[I(ICl)_2]^+$.

The cation $[I(BrCl)]^+$. It enters into the composition of two compounds: $[I(BrCl)][SbCl_6]$ and $[I(BrCl)](SO_3F)$. The first was obtained[41,80] by the interaction of IBr, Cl_2, and $SbCl_5$ in SO_2 (at −78 °C) and the second by mixing equimolar amounts of $[IBr_2](SO_3F)$ and $[ICl_2](SO_3F)$ at 95 °C.[78] It is believed[33,41] that this entails the formation of a disordered mixture of the cations $[IBr_2]^+$, $[ICl_2]^+$, and $[I(BrCl)]^+$ which are in equilibrium

$$2[I(BrCl)]^+\rightleftharpoons[IBr_2]^+ + [ICl_2]^+.$$

The cation $[ClF_4]^+$. The study of the system ClF_5–SbF_5 (Fig.7) led to the observation[186] of three new congruently melting phases containing the cation $[ClF_4]^+$: $[ClF_4].[SbF_6]$ (m.p. 120 °C), $[ClF_4][Sb_2F_{11}]$ (m.p. 64 °C), and $[ClF_4][Sb_4F_{11}]$ (m.p. 62 °C), the last two compounds having very small crystallisation regions. The first compound has two polymorphic modifications (α and β) with a phase transition temperature of approximately 40 °C. The melting point data,[52,123] for the compound $[ClF_4][SbF_6]$, obtained by preparative synthesis, disagree with the more accurate data.[186] It has been established that HF cannot be used as the solvent for the synthesis of this compound.[186] The system ClF_5–HF is distinguished by the complete absence of the miscibility of the components in both liquid and solid states.[187]

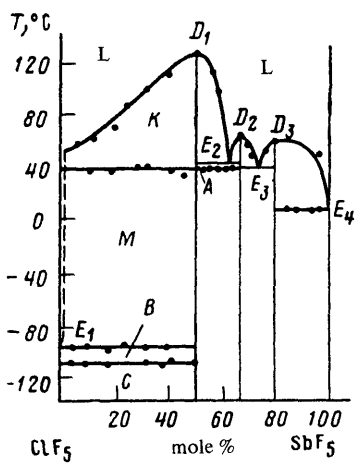


Figure 7. Phase diagram for the system ClF_5–SbF_5:[186] D_1 = $[ClF_4][SbF_6]$; D_2 = $[ClF_4][Sb_2F_{11}]$; D_3 = $[ClF_4].[Sb_4F_{21}]$; A = α-$[ClF_4][SbF_6]$ + $[ClF_4][Sb_2F_{11}]$; B = β-$[ClF_4][SbF_6]$ + α-ClF_5; C = β-$[ClF_4][SbF_6]$ + β-ClF_5; K = α-$[ClF_4][SbF_6]$ + L; M = β-$[ClF_4][SbF_6]$ + L.

The synthesis of $[ClF_4][AsF_6]$ and $[ClF_4][PtF_6]$ is based on the repeated heating and cooling of a mixture of ClF_5 and AsF_5(PtF_6) in the temperature range between −196° and +20 °C.[91,123] The system ClF_5–BF_3 is characterised by the absence of miscibility of the components in both liquid and solid states over the entire concentration range.[188]

The cation $[BrF_4]^+$. In contrast to the previous system, the interaction of BrF_5 and SbF_5 leads to the formation of five new phases (Fig.8), among which only one, $[BrF_4].[Sb_2F_{11}]$, melts congruently (at 81 °C).[189] The low melting point (60–61 °C) observed for this phase elsewhere[113,190] is caused by the presence of impurities.

A general method of synthesis of compounds of halogen cations, incorporating the ion $[BrF_4]^+$, involves the condensation of BrF_5 at −196 °C in a reactor containing the

fluorides or oxides of the elements in the highest oxidation states with subsequent alternate heating and cooling of the reactor. In the last stage of the synthesis, the excess BrF_5 is removed *in vacuo*. The cation halogen compound of tetrafluorobromine (III) with the anions $[Sb_2F_{11}]^-$,[53,61,97] $[AsF_6]^-$,[53] $[SnF_6]^{2-}$,[9,192] and $[RuF_6]^-$ [12] (all in the crystalline state) and also with the anions SO_3F^- [190] and $[PtF_6]^-$ [90,91] (in the form of viscous liquids which do not crystallise at low temperatures) were obtained in this way.

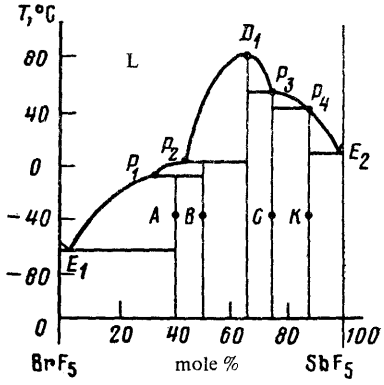


Figure 8. Phase diagram for the system BrF_5–SbF_5:[189] D_1 = dystectic composition $[BrF_4][Sb_2F_{11}]$ (m.p. 81 °C); m.p. of peritectic phases (°C): $P_1 = -8$; $P_2 = 0$; $P_3 = +50$; $P_4 = +40$; E_1, E_2 = eutectic points; $A = 3BrF_5.2SbF_5$; $B = BrF_5.SbF_5$; $C = BrF_5.3SbF_5$; $K = BrF_5.7SbF_5$.

The formation of the cation $[BrF_4]^+$ has not been established in the systems BrF_5–$BF_3(NbF_5, BiF_5)$,[8,97,188] BrF_5–$PF_5(TiF_4)$,[113] BrF_5–UF_6,[9,149] and BrF_5–HF.[9,12,22,88]

The cation $[IF_4]^+$. When IF_5 and SbF_5 interact, three new phases appear (Fig. 9):[192] the congruently melting $[IF_4].[SbF_6]$, the incongruently melting $[IF_4][Sb_2F_{11}]$, and the $IF_5.6SbF_5$ phase whose nature has not been elucidated.

The method of synthesis of the majority of the cation halogen compounds with the cation $[IF_4]^+$ is analogous to that used for $[BrF_4]^+$. The compound $[IF_4][CrF_4.Sb_2F_{11}]$ has been synthesised[98] by the reaction in liquid IF_5 at 60 °C (yield 100%):

$$3IF_5+2O_2[CrF_4\cdot Sb_2F_{11}]=[IF_4][CrF_4\cdot Sb_2F_{11}]+2O_2+IF_7 .$$

The compound decomposes at 153 °C. Compounds with the anions $[SbF_6]^-$,[53,64,108,115,192,193] $[Sb_2F_{11}]^-$,[51] $[PtF_6]^-$,[144,145] and $[CrF_4.Sb_2F_{11}]^-$ [8,98] have been obtained in the crystalline state. The compound $[IF_4](SO_3F)$ is formed in the liquid.[193]

The system IF_5–HF is the eutectic type,[194] the cations $[IF_4]^+$ being detected only in the liquid phase.[9,194]

The cation $[ClF_6]^+$. The synthesis of the cation halogen compounds with the cation $[ClF_6]^+$ proved to be possible only[62] when a powerful oxidant, such as KrF_2, is used under the conditions of cyclic heating from −196° to +20 °C and cooling:

$$ClF_5+KrF_2+AsF_5=[ClF_6][AsF_6]+Kr .$$

The excess ClF_5 used as a solvent increases the yield of the complex, which crystallises without an admixture of the cations $[ClF_4]^+$. The compound $[ClF_6][SbF_6]$ was obtained analogously. The synthesis of $[ClF_6][BF_4]$ is possible only via the exchange reaction of $[ClF_6][AsF_6]$ and $Cs[BF_4]$ in HF on raising the temperature from −196° to +25 °C and subsequent cooling of the mixture to −78 °C.[100] The $Cs[AsF_6]$ residue is separated and $[ClF_6][BF_4]$ is crystallised from the filtrate in 55% yield. The synthesis of $[ClF_6][AuF_6]$ is believed to be possible.[195] According to a series of data,[68,86,99]

$$2ClF_5+2PtF_6=[ClF_6][PtF_6]+[ClF_4][PtF_6]$$
$$6ClO_2F+6PtF_6=[ClF_6][PtF_6]+5(ClO_2)[PtF_6]+O_2$$

take place when mixtures of the reactants are heated slowly from −196° to +25 °C with simultaneous UV irradiation (water–Pyrex filter) for several days. The reaction products could not be fully separated.

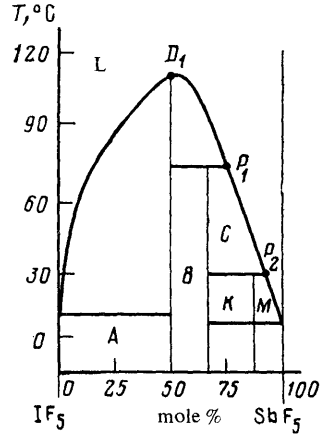


Figure 9. Phase diagram for the system IF_5–SbF_5:[192] D_1 = dystectic composition $[IF_4][SbF_6]$ (m.p. 111 °C); P_1 and P_2 = the peritectic phases $[IF_4][Sb_2F_{11}]$ (m.p. 72 °C) and $IF_5.6SbF_5$ (m.p. 27 °C) respectively; $A = IF_5 + [IF_4].[SbF_6]$; B = mixture of the solid phases D_1 and P_1; $C = [IF_4][Sb_2F_{11}] + L$; $M = IF_5.6SbF_5 + L$; K = mixture of the solid phases P_1 and P_2.

The interaction of the components in the systems ClF_5–F_2–$SbF_5(AsF_5)$ and ClF_5–F_2–BF_3 was not observed at pressures in the range 30–40 atm and temperatures in the range 100–225 °C.[86] Instead of the oxidation of ClF_5 to ClF_7, the former decomposes to ClF_3 and Cl_2 with formation of compounds having the cation $[ClF_2]^+$.

The cation $[BrF_6]^+$. The attempts to synthesise compounds with the above cation by mixing BrF_5, F_2, and $AsF_5(SbF_5)$ were unsuccessful despite the use of increased pressures (125–200 atm) and temperatures (200–250 °C) and varying the molar ratios of the components. Only when a new powerful oxidant KrF_2 was employed, was it possible[60,61,67] to synthesise $[BrF_6][AsF_6]$ and a mixture of $[BrF_6][Sb_2F_{11}]$ with $[BrF_4][Sb_2F_{11}]$. The latter compound is removed from the mixture *in vacuo* at 50 °C. However, after this operation, the composition of the residual cation halogen compounds

becomes indefinite:[67] $[BrF_6][SbF_6].xSbF_5$ ($x < 1$). The reaction involving KrF_2 proceeds in BrF_5 at −196 °C. The excess BrF_5 and KrF_2 are removed by evacuation. The yield of the halogen cation compounds with the ion $[BrF_6]^+$ does not exceed 20%. The reasons for the formation of $[BrF_6][Sb_2F_{11}]$ instead of $[BrF_6][SbF_6]$ remain obscure.

The cation $[IF_6]^+$. Cation halogen compounds containing the anions $[AsF_6]^-$,[6,9,12,56,127,196–198] $[SbF_6]^-$,[66] $[Sb_3F_{16}]^-$,[12,127,197,198] $[BF_4]^-$,[6,127] $[BF(TeOF_5)_3]^-$,[199] and $[AuF_6]^-$ [65] have been obtained with this cation.

A general method of synthesis of the compounds is joint condensation in a single reactor at −196 °C of the initial reactants with subsequent increase of temperature to 0 °C; the remaining reactants are removed by evacuation.[56,59,127,200,201] If one of the reactants (IF_7) boils before the other (SbF_5) becomes liquid, then the reaction is carried out by passing gaseous IF_7 through a melt of SbF_5 at 20 °C.[127] The structure of $[IF_6][Sb_3F_{16}]$ has not been ultimately elucidated.

A reaction which takes place even at 20 °C but leads to the formation of a mixture of two solid phases has been proposed for the synthesis of the compound with the anion $[AuF_6]^-$:[65]

$$3IF_5+4O_2[AuF_6]=3[IF_6][AuF_6]+4O_2+AuF_3 .$$

VI. APPLICATIONS

The cation halogen compounds have a multiplicity of novel physical and chemical properties which lead to a wide variety of possibilities in their practical use. In the first place, being strong oxidants, they have been recommended as components of rocket fuels and in the technology of the processing of nuclear materials.[9]

The compounds $[Cl(ClF)][AsF_6]$, $[ClF_4][SbF_6]$, and $[BrF_2][SbF_6]$ proved to be excellent fluorinating agents at comparatively low temperatures in closed reactors and at low pressures developed in the process;[122,141,150,162] $[BrF_6]$. $[AsF_6]$ is more effective than F_2 under the usual conditions, oxidising, for example Xe and O_2:

$$[BrF_6][AsF_6]+Xe=(XeF)[AsF_6]+BrF_5 ,$$
$$[BrF_6][AsF_6]+O_2=O_2[AsF_6]+BrF_5+0.5F_2 .$$

The effectiveness of the halogen cation compounds in organic synthesis has been mentioned frequently.[202,203] In particular, it is technologically convenient to synthesise fluorinated aromatic derivatives of iodine(VII) with the aid of $[IF_4][SbF_6]$.[203] The authors believe[203] that the halogen cation compounds lead to new possibilities for the synthesis of compounds containing Ar–Hal (Hal = I, Br, or Cl). The halogen cation compounds $[Cl(ClF)][AsF_6]$, $[ClF_2][AsF_6]$, $[ClF_4][SbF_6]$, and similar compounds can be used as solid sources of chlorine fluorides and devices for their storage. When necessary, these fluorides can be regenerated in a pure form.[141]

The most promising application of the halogen cation compounds is the synthesis of new substances by mixing solutions containing the corresponding halogen cation compound (Lewis acid) and the halogenate anion (Lewis base). The solvent in this instance is the interhalogen compound whose autoionisation leads to the formation of the cation and anion of the reactant. An example is provided by the reaction

$$[BrF_2][PF_6]+Ag[BrF_4]=Ag[PF_6]+2BrF_3 .$$

Numerous complexes, whose synthesis had been regarded as impossible previously, have been obtained by this method.[12,113,115,155,156,160,162,163] The reversibility of some of the reactions and the solvolysis of the product are complications in synthesis of this kind.

The exchange reactions involving the complex cations may be used for synthesis:[12,204]

$$[BrF_2][AuF_4]+SeF_4=(SeF_3)[AuF_4]+BrF_3 .$$

These reactions can be employed also for the purification of chemical fluorides.[205]

The determination of chemically combined oxygen in minerals, raw materials (ores), and metal oxides and phosphates is a difficult analytical problem whose solution has become possible after the appearance of the halogen cation compounds. In particular, when thermostable oxides (ThO_2, Al_2O_3, ZrO_2, etc.) and phosphates are heated with $[BrF_2][SbF_6]$ to temperatures above 330 °C, oxygen is evolved quantitatively.[12,122] The same reagent has been proposed[206] for the direct quantitative determination of chemically combined oxygen in alcohols and aliphatic and aromatic acids.

The reaction

$$Rn+[IF_6][SbF_6]=(RnF)[SbF_6]+IF_5$$

has been recommended[66,207] for the separation of a mixture of Rn, Xe, and Kr, for the determination of Rn in air, and for the removal of the radioactive radon impurity in air. The use of halogen cation compounds makes it possible to eliminate radon and other carcinogenic substances (^{218}Po, ^{214}Po, ^{214}Pb, and ^{214}Bi) almost completely from air in uranium mines.[207] The xenon evolved on dissolution of spent radioactive fuel may be utilised by means of reactions involving the formation of the adducts $2IF_5.XeF_2$ [208,209] and $IF_5.XeF_4$.[210,211]

VII. CONCLUSIONS

It follows from the data presented above that, in the direct synthesis of halogen cation compounds with halide ligands, halogens and diatomic interhalogen compounds should be used only together with powerful oxidants. Otherwise molecular ligands appear in the inner sphere with the complex-forming agent in the +1 oxidation state, for example, $[I(I_2)_2]^+$ and $[I(ICl)_2]^+$.[212–214] The halogen cation compounds with the cations $[ICl_4]^+$ and $[IBr_4]^+$ have not so far been obtained owing to the extreme instability of ICl_5 and IBr_5.[215]

The halogen cation compounds examined in this review are not distinguished by a wide variety of anions. The anions are mainly $[AsF_6]^-$, $[SbF_6]^-$, $[SbCl_6]^-$, $[BF_4]^-$, $[AlCl_4]^-$, and a few others. The properties of powerful halide ion acceptors can also be manifested by the fluorides and chlorides of elements capable of being converted into acido-complexes.

The dependence of the stability of the halogen cation compounds on the nature of the anions has not so far been accounted for. For example, BF_3 exhibits an appreciable accepting capacity in relation to fluoride ions, but it does not interact with either ClF_5 or with BrF_5 to form the cations $[ClF_4]^+$ and $[BrF_4]^+$.[188] The most stable halogen cation compounds contain almost always the anion $[AsF_6]^-$. The appearance in the anion of bromide or iodide ligands, which are readily oxidised, precludes the synthesis of the halogen cation compounds. Such ligands destabilise the cations, reconverting them into halogens or interhalogen compounds.

The more exothermic the formation reactions of anions of the type,

$$SbF_5+F^- \rightleftharpoons [SbF_6]^-,$$

the more stable should apparently be the resulting halogen cation compounds. Thus their stabilisation is also promoted by the electrolytic dissociation of interhalogen compounds[213]

and by the ready solubility of the latter in Lewis acids functioning as halide ion acceptors. It has been established that the energy of abstraction of fluoride ions from halogen fluorides diminishes from ClF_5 to IF_5. The stability of the halogen cations associated with the same anion increases in the same direction:

$$[ClF_4]^+ < [BrF_4]^+ < [IF_4]^+.$$

The interaction of halogen fluorides and Lewis acids in the liquid phase is as a rule rapid and proceeds with a high yield.

Little is known about the mechanism of the formation reactions of the halogen cation compounds. The conditions governing the equilibria in solutions between the ions $[I_2]^+$ and $[I_3]^+$ and between $[I_3]^+$ and $[I_4]^{2+}$ or the causes preventing the appearance of the cations $[I_5]^+$ in the system I_2–$S_2O_6F_2$ or the cation $[I_3]^+$ in the system I_2–$AlCl_3$–$NaCl$ [214] and favouring their formation in the system I_2–ICl–$AlCl_3$ have not been elucidated. The possibility of reactions of the type

$$3ICl \rightleftharpoons [I(ICl)]^+ + [ICl_4]^- \quad \text{or} \quad 3ClF \rightleftharpoons [Cl(ClF)]^+ + [ClF_2]^-$$

is open to doubt. The dismutation

$$3ClF \rightleftharpoons ClF_3 + Cl_2 \quad \text{or} \quad 3ICl \rightleftharpoons ICl_3 + I_2$$

followed by other reactions is more likely. It may be that in this process one of the stages involves an elimination reaction with formation of radicals. The appearance of the latter, for example $Cl_3^\cdot$, $ClF_2^\cdot$, [212] or Cl_4^+, [120] has been frequently mentioned.

A fundamentally new method of synthesis of halogen cation compounds is that involving the explosive interaction between two different halides of the same metal. Single crystals of $[ClF_6][CuF_4]$, for example, have been obtained by this method from a mixture of CuF_2 and $CuCl_2$. [216]

In conclusion, it should be noted that the study of the chemistry of the halogen cation compounds is only just beginning and much still remains to be done before it occupies its due place in modern inorganic chemistry.

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