RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

November 1965

U. D. C. 543.217 : 546.311 : 546.133

ANIONHALOGENATES OF THE ALKALI METALS AND AMMONIUM

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I. INTRODUCTION

Anionhalogenates is the name given to complexes of the type $M[X'_nX''_mX'''_k]$, where M^+ is the cation of an alkali metal, ammonium, or thallium(I) or the singly-charged cation of an organic base, and X_j^i represents various halogens constituting a complex singly-charged anion†. Usually $n + m + k = 3$, 5, 7, or 9. Anionhalogenates containing four different halogens are unknown.

† In some instances doubly- and triply-charged metal ions can be the cations.

These complexes are often called polyhalide compounds (polyhalogenides), which is not completely accurate, as the latter could also include some polynuclear compounds, for example $K_2[Mo_3Cl_4Br_4].2H_2O$, $Ta_6Br_{14}.7H_2O$, etc. Cationhalogenates (not considered in the present review) are also known; they include a small number of complexes with the general formula $[X'_nX''_m]MX'''_k$, where M = Sb, Bi, Nb, Ta, Ti, and a few other elements, X'''_k is fluorine or chlorine, and X'_n and X''_m are different halogens.

The terminology we have suggested is not completely new. Zintl and Kaiser[1] recommended that compounds of the alkali metals with the elements occupying the four nearest places before each of the noble gases in the Long Periods should be called "polyanion salts". Fialkov[2] also classified polyhalides into cationic and anionic complexes, emphasising that the latter "have much in common with the halogeno-salts which are formed by other non-metallic and multivalent elements", but Grinberg[3] considers it more correct to term, for example, compounds of the type $M[ICl_4]$ tetrachloroiodates.

It is characteristic of anionhalogenates that their complex anion is entirely constructed from halogens with iodine or bromine most often as the central atom. In ions containing different halogens, the more electronegative (the lightest) halogens always are coordinated around the less electronegative (heavier) halogen, which is located at the centre of the complex anion.

It is thought[2] that the formation by any substance of complexes of anionic or cationic type depends considerably on the ability of this substance to show either donor or acceptor properties with respect to the halogens. Thus in reacting with antimony pentafluoride, bromine trifluoride is a donor of fluorine and therefore gives a cationic complex $[BrF_2]^+$ in the compound $[BrF_2][SbF_6]$; however, in reacting with potassium fluoride bromide trifluoride behaves as an acceptor of fluorine, by forming the anionic complex $[BrF_4]^-$ in potassium tetrafluorobromate $K[BrF_4]$.

As Wells and Wheeler[4,5] have already proposed, anionhalogenates are classified according to the number of atoms

of halogens in the molecule of the compound, into trihalogenides, pentahalogenides, etc. Such a formal classification is scarcely justified, since it does not reflect the physicochemical and structural features of the anionhalogenates. We consider it more correct, in conformity with Werner's views[6], to divide the anionhalogenates into two large groups: the isopolyhalogenates (in Werner's terminology, "pure polyhalogenides") and heteropolyhalogenates (in Werner's terminology, "mixed polyhalogenides"). In the last group, taking into account stereochemical data, it is desirable to distinguish between heteropolyhalogenates with a linear anion and heteropolyhalogenates with a square planar anion.

Anionhalogenates are not just of purely scientific interest; they are beginning to find ever-increasing use, both in the technology of the separation of alkali metals with very similar properties, and also in the preparation of extremely pure rubidium and caesium salts[7-14].

II. GENERAL CHARACTERISTICS OF ANIONHALOGENATES

The anionhalogenates are a class of complexes whose stability in the solid state and in solution is greatly determined by the polarisation interaction of the ions and molecules, and consequently by the dimensions and charge of both the outer-sphere cation and the central atom. It is known, for example, that small cations (lithium and sodium), which are surrounded by an electric field of rather considerable potential, coordinate the most electronegative ligands of the complex anion, thus destroying the latter. Therefore all the attempts to isolate from solution anhydrous anionhalogenates of lithium and sodium were unsuccessful and yielded only the simple halides of these metals. For the same reason, anionhalogenates with doubly-charged‡ (and especially triply-charged) cations are almost unknown. Multicharged ions can here only enter into the composition of anionhalogenate molecules when they are capable of forming large complex cations, for example, $[Be(H_2O)_8]^{2+}$, $[Co(NH_3)_6]^{3+}$, etc., which exhibit low polarising power and therefore have little effect on the coordination of the ligands in the complex anion. Thus Ephraim and Mosimann[17] prepared $[Co(NH_3)_6][I(I)_2]_3$ and salts of tetrachloroiodic acid with beryllium(II), zinc(II), manganese(II), cobalt(II), nickel(II) and the alkaline earth metals with the general formula $[M(H_2O)_8][ICl_4]_2$.[18,19] For this reason when lithium and sodium form anionhalogenates it is always with molecules of solvent, which stabilise the complex owing to the decrease in the energy of interaction of the cation with one of the ligands.

The thermal stability (see Table 1) of the anionhalogenates of a single alkali metal is determined by the nature of the complex anions. The alkali metal diiodoiodates and dibromoiodates have the greatest thermal stability. The thermal stability of the anionhalogenates is also determined by the size of the outer-sphere cation (see Table 1): it increases with the radius of the cation and therefore the caesium salts are the most stable of the alkali metal anionhalogenates. From the standpoint of the electrostatic theory the thermal stability of the anionhalogenates is the greater, the weaker the electric field of the cation, that is, the less its ability towards counterpolarisation, which weakens the chemical bond between the halogen atoms[3].

‡ With the exception[15,16] of $Ba[IF_4]_2$ and $Ba[BrF_4]_2$.

TABLE 1. Dissociation pressures of anionhalogenates, mmHg.

Compound	Temperature, °C					Reference
	25	50	100	150	200	
$K[I(I_2)]$	—	—	115	450	—	20
$(NH_4)[I(I_2)]$	$1.6\cdot10^{-3}$	—	—	760(146°)	—	21,22
$Rb[I(I_2)]$	—	—	2.97	38.9(160°)	172.4	20,23
$Cs[I(I_2)]$	$7.4\cdot10^{-3}$	—	—	12	126	20,24
$K[ICl_4]$	1.3	6.0	186.6	—	—	25,26
$(NH_4)[ICl_4]$	—	9.8	35.2	51.2	60.3	26
$Rb[ICl_4]$	—	5.3	22.6	43.4	54.8	26
$K[IBr_2]$	2.5	5.5	19(80°)	—	—	27,28
$[K(H_2O)][IBr_2]$	11	31	232	—	—	28,29
$(NH_4)[IBr_2]$	—	6	45	387	—	20
$Rb[IBr_2]$	—	—	33	248	760(186°)	20
$Cs[IBr_2]$	—	—	—	39	203	20
$[K(H_2O)][ICl_2]$	12	48	276	704(136°)	—	20,27
$Rb[ICl_2]$	—	—	96.5	507	—	20
$Cs[ICl_2]$	—	—	24(112°)	114	563	20
					760(209°)	
$K[I(BrCl)]$	13.5	48	166(79°)	—	—	27
$Cs[I(IBr_2)]$	$4.8\cdot10^{-3}$ (6°)	—	—	290(172°)	655	20,30
$(NH_4)[Br(Br_3)]$	7	32	—	—	—	20,31
$Rb[Br(Br_3)]$	7(35°)	18	565	—	—	20,32
$Cs[Br(Br_3)]$	—	—	132	760(148°)	—	20
$(NH_4)[BrCl_2]$	105	484	—	—	—	20
$Rb[BrCl_2]$	27	60	760(93°)	—	—	20
$Cs[BrCl_2]$	—	—	132	760(138°)	—	20
$Rb[Br(BrCl)]$	39	80	760(81°)	—	—	20
$Cs[Br(BrCl)]$	—	15(54°)	270	760(124°)	—	20

This partly explains why complicated complex anions such as $[I(I_2)_4]^-$, $[Br(Br_2)_2]^-$, $[I(I_3Cl)]^-$, $[I(I_5Br)]^-$, etc. are unstable in aqueous solutions of caesium halides but comparatively readily form stable, well-crystallising compounds with large singly-charged organic cations, for example, tetramethylammonium and trimethylphenylammonium. Symmetrically constructed anionhalogenate complex ions with iodine as the central atom are always the most stable (see Table 1). We must note in passing that Ephraim's results[20] on the thermal stability of many anionhalogenates are rather too high owing to the imperfections of the method used. All the alkali metal anionhalogenates decompose on heating close to the melting point but when heated in a sealed capillary they melt at quite definite temperatures.

In aqueous solutions the anionhalogenates undergo complex transformations[33-35]. At first the compound dissociates:

$$Rb[IBr_2] \rightleftharpoons Rb^+ + [IBr_2]^-.$$

Then the complex anion decomposes into its original components:

$$[IBr_2]^- \rightleftharpoons IBr + Br^-.$$

After this, the interhalogen compound formed undergoes hydrolysis:

$$IBr + H_2O \rightleftharpoons IOH + H^+ + Br^-;$$
$$5IOH \rightleftharpoons 2I_2 + IO_3^- + H^+ + 2H_2O.$$

From the increase in the degree of hydrolysis at 25° in 0.05 M aqueous solutions, the complex anions can be arranged in the following series:

$$[ICl_4]^- < [IBr_2]^- < [I(BrCl)]^- < [ICl_2]^-.$$

Moderately concentrated aqueous solutions of anionhalogenates which contain iodine show a strong acid reaction, although it is impossible to detect the liberation of elemental iodine even by spectrophotometry. Evidently here the hydrolysis of the interhalogen compound stops at

the stage of formation of hypoiodous acid, which is stabilised under certain conditions by the addition of a neutral molecule of an interhalogen compound, for example, IOH.IBr.

The hydrolysis is accelerated when the pH is increased and in alkaline solutions it goes to completion, with formation of the corresponding halide, iodate, and iodine (or iodide)[2]. The hydrolysis is suppressed by the introduction into the solution of acids, halogens, iodates, or halides of the alkali metals.

A point worth remembering is that in aqueous solutions some anionhalogenates also undergo partial disproportionation:

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

The solvolytic reactions of anionhalogenates have been little studied and the above facts really exhaust all our present knowledge in this field.

The theory of the absorption spectra of the anionhalogenates which is now being developed allows for the use of the p-orbitals of iodine and bromine central atoms in forming bonds[28,36-38]. The position of the absorption bands of the anionhalogenates is almost independent of the outer-sphere cation and solvent and depends mainly on the corresponding energy transitions characteristic of the type of chemical bond involved. Spectrophotometric investigations[39-48] of various solutions of diiodoiodates indicate that the chromophoric group I^+-I^- corresponds to two absorption bands, at 290 and 360 mμ. The chromophoric group Br^+-Br^- in dibromobromates characterises the absorption bands at 265 and 395 mμ,[40,42,49] and the I^+-Br^- chromophoric group in dibromoiodates corresponds to absorption bands[40,42] at 256 and 380 mμ. Analogously, the I^+-Cl^- bonds in dichloroiodates have absorption bands at 227 and 340 mμ,[40,42,50-52] and the Br^+-Cl^- bonds in dichlorobromates absorption bands at 254 and 385 mμ.[42] In its energy transitions the Br^+-Cl^- bond appears to be close to the I^+-Br^- bond. The successive replacement of the ligands (iodine atoms) in diiodoiodates by bromine and chlorine leads to a displacement of the absorption band at 290 mμ to shorter wavelengths.

The absorption spectra of anionhalogenates with two different ligands usually show absorption bands corresponding to a few chromophoric groups. For example, water-alcohol solutions of bromochloroiodates have absorption bands at 220, 255, and 455 mμ;[53] in other solvents, the absorption band characteristic of the I^+-Cl^- chromophoric group can be displaced to 237 mμ,[40] and sometimes there is superposition of the absorption bands of the I^+-Cl^- and I^+-Br^- chromophoric groups and the formation of an inflection at 230-250 mμ.[42] In trifluoroacetic acid the absorption band of tetramethylammonium bromochloroiodate, for example, is at 486 mμ.[54] The absorption spectra of the iodochloroiodates show all the frequencies characteristic of both the I^+-I^- and the I^+-Cl^- bonds[40,42,51]. A somewhat different absorption spectrum is observed for bromochlorobromates and iodobromoiodates, where perturbations in the Br^+-Br^- and I^+-I^- chromophoric groups dominate and therefore in the spectra of these compounds there are only absorption bands at 265 and 400 mμ [42,55] and 280 and 360 mμ respectively[40,42].

The dependence of the molar extinction coefficient on the nature of the solvent shows that the latter play an important part in the corresponding energy transitions of the excited complex anion. Thus, in alkali metal diiodoiodates and dibromoiodates, as the dielectric constant of the solvent is reduced the molar extinction coefficient for the absorption bands at 290 and 256 mμ increases linearly. Almost the same thing is observed for the absorption bands at 360 and 380 mμ. Such a linear dependence is not observed for dichloroiodates and bromochloroiodates; here there is another relation: the molar extinction coefficient of the complexes increases (although also not proportionately) with the dipole moment of the solvent.

A study of the infrared and Raman spectra[56,57] allowed the force constants of the bonds of the ions $[Br(Br_2)]^-$, $[ICl_2]^-$, $[ICl_4]^-$, and $[BrCl_2]^-$ to be calculated. It was found that the force constants for the interaction between bonds at an angle of 180° in these ions, equal to 0.26×10^{-5}-0.36×10^{-5} dyn cm^{-1}, can be arranged in a sequence which corresponds qualitatively with the thermal stability sequence: the less stable anionhalogenates correspond with the smaller force constants.

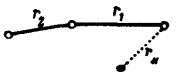
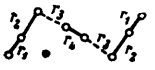
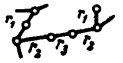
The nature of the chemical bonds in anionhalogenates is discussed mainly in terms of localised covalent bonds (the localised electron pairs method) and molecular orbitals (delocalisation of the p-electrons of the halogen atoms)[4,58,59]. Electrostatic theory, which is more graphic, is also sometimes used[3,60-65]. For example, the formation of a bond between the I^- ion and an iodine molecule can be explained by the polarisation of the latter by the I^- ion, the creation of a dipole, and subsequent ion-dipole interaction. This leads to an increase in the interatomic distance in the iodine molecule, from 2.67 Å to 2.82-2.90 Å (see Table 2). The decrease in the electrostatic interaction between the cation and an $[I(I_2)]^-$ anion, associated with the increase in the dimensions of the cation (replacement of ionic bonds by covalent), leads to a decrease in r_1 and an increase in r_2. In tetraphenylarsonium diiodoiodate, for example, the complex anion is already becoming strictly symmetrical ($r_1 = r_2 = 2.90$ Å) with the greatest value of r_k (see Table 2). The electrostatic interaction of small cations with the I^- ion is so strong that a complex anion is not formed. For that very reason, as we have already mentioned, potassium diiodoiodate exists only as a crystalline hydrate in which the water forms part of an aquocation[66].

From the standpoint of the molecular orbital method[36,37,66,73,77,82-84], the bonding in anionhalogenates is explained by the large value of the overlap integral of the p-orbitals, which are extended in the direction of the bonds. The molecular orbitals here are represented by linear combinations of the most distant p-orbitals of the halogen atoms. The delocalisation energy calculated for different configurations of the number of halogen atoms involved, was least for the structures of the anionhalogenates which were actually observed. The large value of the integral of the interaction perpendicular to the position of the various p-orbitals of one halogen atom in relation to the p-orbital of another atom naturally explains the fact that all the valence angles in the anionhalogenates are close to 90°, or to 180° (see Tables 2 and 3).

Some remarks must be made about several anionhalogenate structures. The complex Cs_2I_8§ or $2CsI_3.I_2$ [76] consists of two asymmetric $[I(I_2)]^-$ ions which are weakly interacting with one molecule of iodine[4,70,76]. The complex anion $[I(I_2)_2]^-$ or $[I_5]^-$ has a planar, V-shaped form (Table 2)

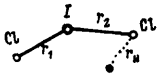
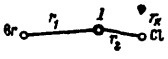
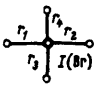
§ The diamagnetism of CsI_4 [85] necessitated doubling the formula, since otherwise this compound would contain an odd number of electrons and be paramagnetic.

TABLE 2. Interatomic distances in isopolyhalogenates.

Compound	Form of structural species	Interatomic distances r_1	r_2	r_3	r_k	Angle between bonds, deg	Reference
$NH_4[I(I_2)]$		3.10	2.82	—	3.6	177	66,69
$Cs[I(I_2)]$		3.03	2.83	—	3.70	176	21,28,70—72
$[As(C_6H_5)_4][I(I_2)]$		2.90	2.90	—	—	176	73,74
$(Br^-)[(CH_3)_3NH]_3[Br(Br_2)]$		2.54	2.53	—	—	171	4,75
Cs_2I_8		2.85	3.00	3.42	3.85	∢ r_1r_2 177 ∢ r_2r_3 81 ∢ r_3r_4 175	76
			r_4=2.80				
$[(CH_3)_4N][I(I_2)_2]$		2.82	3.17	—	—	∢ r_1r_2 175 ∢ r_2r_2 95	77,78
$[(C_2H_5)_4N][I(I_2)_3]$		2.904	3.435	2.735	—	∢ r_1r_1 180 ∢ r_1r_2 80.5 ∢ r_2r_3 176	4,79,80
$[(CH_3)_4N][I(I_2)_4]$		2.67	3.43	3.24	—	∢ r_1r_2 168 ∢ r_2r_3 156 ∢ r_3r_4 178 ∢ r_3r_4 85 ∢ r_3r_4 89 ∢ r_4r_5 175 ∢ r_5r_3 87 ∢ r_3r_5 169	4,81
		r_4=3.18		r_5=2.90			

Symbols: o atom of iodine (or bromine); • cation; r_k distance from cation to nearest halogen.

TABLE 3. Interatomic distances in heteropolyhalogenates

Compound	Form of structural species	Interatomic distances r_1	r_2	r_k	Angle between bonds, deg	Reference
$[(CH_3)_4N][ICl_2]$						4, 69, 86
$[(C_4H_{10}N_2)HClH^+][ICl_2]$		2.34	2.34	—		87
$Cs[ICl_2]$		2.47	2.69	3.23	180	28, 86, 88
$[PCl_4]\cdot[ICl_2]$		—	—	—		89
		2.36	2.36	—		
$(NH_4)[I(BrCl)]$		2.50	2.38	3.35	178	90, 91
$K[ICl_4]\cdot H_2O$		2.53	2.47	3.27	89—90	65, 92, 93
		r_3=2.60		r_4=2.42		
$K[BrF_4]$		1.81—1.88	—	2.84		4,94—96

Symbols: see Table 2.

in which the interaction between the iodine central atom and the iodine molecules is much stronger[77] than in the $[I_3]^{2-}$ ion. In the crystal lattice of the complex compound $M[I(I_2)_3]$ each $[I(I_2)]^-$ ion is surrounded by four iodine molecules and each iodine molecule by two $[I(I_2)]^-$ ions (unit cell)[4,79].

In ammonium bromochloroiodate the cation is coordinated with four chlorine atoms and four bromine atoms, which are arranged alternately at the corners of a greatly distorted cube (see Table 3). Hence the structure of this complex is reminiscent of the structure of caesium chloride[90]. Calculation of the structure of the $[I(BrCl)]^-$ ion by the molecular orbital method showed that a linear configuration of this complex anion with a centrally situated iodine atom is the most favourable energetically[97].

The $[ICl_4]^-$ ion has a slightly pyramidal configuration with an iodine atom at the apex of the pyramid (see Table 3). The chlorine atoms lie in a plane 0.02–0.05 Å from the iodine atom and occupying the corners of a somewhat distorted square[82,92,93]. The potassium ions are situated between the planes of such squares and are coordinated with six chlorine atoms at a mean distance of 3.32 Å. Apparently the size of the potassium cation is limiting for the formation of a sufficiently stable crystal lattice of potassium tetrachloroiodate. Hence in all the anionhalogenates which have been considered the angles between the bonds are approximately 90° and 180° and the interatomic distances are always greater than the sum of the covalent radii; this is expressed especially sharply in the isopolyiodates (see Tables 2 and 3).

The results of X-ray structural analysis and studies of isotopic exchange reactions of the halogens[98], which show the equality of all the bonds in the complex anion, provide a basis for assuming that in the latter the central atom is

a positively charged bromine atom or an iodine atom with a valency electron orbital displaced towards the ligands [2,37,38,99]. This is also suggested by the formal charges of the halogens which are constituents of the complex anion. Thus the charges of the iodine, bromine, and chlorine atoms in the $[I(BrCl)]^-$ ion are respectively [97] +0.07, -0.045, and -0.62. The formal charge in the $[I(I_2)]^-$ ion for the two extreme iodine atoms is -0.5 whereas for the central atom it is almost zero. In the $[ICl_2]^-$ ion the formal charge of each chlorine atom [4,37] is -0.55, and that of the iodine is +0.11. In the $[ICl_4]^-$ ion the chlorine atom has a formal charge of -0.52 and the iodine atom +1.07.

In several chemical properties there is great similarity between the halogens and cyanogen $(CN)_2$ and thiocyanogen $(NCS)_2$, which may be able to form both independent complexes with the alkali metals analogous to the anionhalogenates, for example $Rb(NCS)_3$, and also mixed complexes in which the halogens participate.

III. ISOPOLYHALOGENATES

Difluorofluorates

The alkali metal difluorofluorates, which contain the anion $[F(F_2)]^-$, have not been prepared. Repeated attempts to make them [100-107] by the action of fluorine free of hydrogen fluoride on the alkali metal chlorides, bromides, and iodides at 15–250° usually led either to the production of compounds with a variable fluorine concentration, for example, $RbF_{1.96-1.98}$, or to the isolation of compounds of the type $M[ClF_4]$ and $M[IF_6]$.

Dichlorochlorates

The alkali metal dichlorochlorates have also not yet been obtained. Various attempts to isolate them from aqueous solutions were unsuccessful [32,108-115] evidently on account of the low degree of conversion (0.74%) of Cl^- ions into $[Cl(Cl_2)]^-$ ions in aqueous hydrochloric acid solutions by the reaction:

$$Cl_2(gas) + Cl^- \rightleftharpoons [Cl(Cl_2)]^-.$$

Zimmerman and Strong [113] found the instability constant of the $[Cl(Cl_2)]^-$ ion to be 5.23. The formation of the complex anion is possible also during the dissociation of iodine trichloride by the equation $ICl_3 \rightleftharpoons I^+ + [Cl(Cl_2)]^-$. On dilution of the solution the $[Cl(Cl_2)]^-$ ion decomposes with evolution of chlorine [115].

Solid dichlorochlorates have been obtained only with large cations, such as tetramethylammonium, tetraethylammonium, etc. [116]

Dibromobromates

These are a more stable class of compounds than the dichlorochlorates. Thus, Ray [117] isolated hydrogen dibromobromate $H[Br(Br_2)]$ from a concentrated solution of bromine in 1.5 *N* hydrobromic acid below 0°, as yellow, extremely unstable crystals. As long ago as 1903, Rikhter-Rzhevskaya [118] suggested the formation of a compound in the $HBr-Br_2-H_2O$ system. The heat of formation of the complex acid at 25° is 1.29–2.03 kcal $mole^{-1}$. [49,117,119-121]. Therefore the absence [122] of compounds of the type HBr_n in the $HBr-Br_2$ system below -50° is improbable.

Many investigators [109,123-133] have studied the equilibrium:

$$Br^-.aq + Br_2(liquid) \rightleftharpoons [Br(Br_2)]^-.aq.$$

It was found that the equilibrium constant determined either by the distribution of bromine between carbon tetrachloride and aqueous solutions (0.1–0.5 moles per 1000 g H_2O) [109,123,124,130,131] or from the solubility of bromine in aqueous 0.01–1.0 *N* solutions of sodium and potassium bromides [125-130,132,134,135] is 16–20.7 $mole^{-1}$ litre at 25–33°; the most accurate results [125] give 16.0 $mole^{-1}$ litre at 25°.

Ammonium, rubidium, and caesium dibromobromates have been isolated as solids but the existence of potassium and sodium dibromobromates has been established only in aqueous solutions. The instability constants obtained by various investigators [49,120,127,134,136,137] for aqueous solutions of sodium and potassium dibromobromates at 0–25° range from 4.4×10^{-2} to 6.2×10^{-2}.

In studying the $KBr-Br_2-H_2O$ system at 0°, 25°, and 85°, Harris [138] and Zernike and coworkers [139] found only the crystalline hydrate $KBr_6.1.5H_2O$¶, which separates from solutions rich in bromine as long, red needles, m.p. 25.85°. An analogous sodium compound was not obtained. These reliable investigations [138,139] raise doubt about the earlier reports [20,114,130,131,140-142] of the possibility of obtaining at 0–85° potassium dibromobromate and tetrabromobromate as individual chemical compounds. The existence of a series of potassium polybromobromates in aqueous solution is postulated, particularly the tetrabromobromate [135], with an instability constant of 2.46×10^{-2}. Evidently, during the separation of the polybromobromates from aqueous solutions destruction of the aquocation occurs, with simultaneous breakdown of the molecule; this is shown indirectly by the fact that dry potassium bromide does not react with bromine [143].

Ammonium, rubidium, and caesium dibromobromates are usually obtained by the addition of bromine, in slight excess (2–3%) of the stoichiometric quantity, to hot, concentrated, aqueous solutions of the bromides. On cooling the solution to 0°, very hygroscopic, orange-red crystals separate [5,21,108,143-145]. These complexes can also be obtained by a dry method – either by heating stoichiometric proportions of the alkali metal bromide and bromine until a melt is formed [31,32,143,145], or by the action of bromine vapour on the bromides [143].

Caesium dibromobromate was the only compound observed in a study [147] of the $CsBr-Br_2-H_2O$ system at 0° and 25°. The compounds taken earlier [31,146] to be $Cs[Br_4]$ and $Cs[Br(Br_2)_2]$ do not exist and the solid phase which was then isolated must be considered to be a mixture of bromine-10-water and caesium dibromobromate; Rae [145] and Cremer and Duncan [148] have also noted that it is impossible to obtain $Cs[Br_4]$.

Ether and absolute ethanol decompose ammonium, rubidium, and caesium dibromobromates [33,149] with precipitation of the corresponding bromide. Complex anions containing more than three bromine atoms can exist in solution, from which they can be isolated as compounds with large organic cations. For example, tetramethylammonium octabromobromate is known [150]; it melts congruently at 56.7°.

¶ Because of the diamagnetism of $KBr_6.1.5H_2O$, the formula $2KBr.5Br_2.3H_2O$ was proposed for it.

Diiodoiodates

These are the most studied of all the alkali metal anion-halogenates. Hydrogen diiodoiodate was first obtained as a solid film[46] and then as red crystals on cooling a concentrated solution of iodine in 1.5 *N* aqueous hydriodic acid to -4°.[117] The compound $H[I(I_2)].4C_6H_5CN$ is also known[151].

The equilibrium $I^- + I_2(solid) \rightleftharpoons [I(I_2)]^-$ has been studied frequently[39,152-162] in aqueous and non-aqueous solutions. The instability constant of the $[I(I_2)]^-$ ion, determined at 25° from the distribution of iodine between the aqueous phase and organic solvents (carbon disulphide, carbon tetrachloride, nitrobenzene, etc.) was found to be 1.3×10^{-3}–1.43×10^{-3} for 0.03–1.0 *N* KI solution[59,124,152,153,157,158,163-165]. The heat of the reaction $I_2(solid) + I^-.aq \rightleftharpoons [I(I_2)]^-.aq$ at 25° is 0.893 kcal mole^{-1}.[166-169] The heats of formation of the alkali metal and ammonium diiodoiodates in aqueous solutions at 10–20° increase with the atomic weight of the cation[153].

In addition to the diiodoiodate anion, the presence of the ions $[I_{14}]^{3-}$, $[I_4]^{2-}$, and $[I_6]^{2-}$ in aqueous solutions has also been established[155]; their instability constants at 20–25° are 4.5, 1.2×10^{-2}, and 1.6×10^{-6} respectively. However, complexes with the first two anions could not be isolated from the solutions; the third anion is evidently a dimer of the $[I(I_2)]^-$ ion, as Job suggested[49,170].

Study of the electrical conductivity of solutions of the alkali metal iodides and iodine in nitrobenzene have indicated the possible existence of di-, tetra-, hexa-, and octa-iodoiodates[160,161,171].

Lithium diiodoiodate was obtained only as the double salt [sic] with benzonitrile, $Li[I(I_2)].4C_6H_5CN$, which forms[151] dark green acicular crystals unstable in moist air and melting at 92.5°. The analogous lithium diiodoiodate–*o*-toluonitrile compound is known[151]. According to Dawson[161,171] the formation of lithium tetra-, hexa-, and octa-iodoiodates is possible in nitrobenzene saturated with iodine.

Free sodium diiodoiodate has not been isolated. Only sodium iodide dihydrate, with iodine as impurity, crystallises from solutions containing sodium iodide and iodine at 25°.[172-175] On lowering the crystallisation temperature to 10–12°, a product separates which Grace[176] thought to be sodium diiodoiodate tetrahydrate. A study[177] of solubility in the sodium iodide–iodine–water system at 0° showed the absence of solid phases corresponding to sodium diodoiodate; the compounds obtained were the double salts $NaI.Na[I(I_2)].6H_2O$ and $Na[I(I_2)].Na[I(I_2)_2].4H_2O$. The later results of Briggs and coworkers[178], who studied the same system at 0° and -15° support the existence of rather complex solid phases, of low stability and greatly hydrated, of the type $Na_4I_{14}.(13-15)H_2O$, $Na_5I_{11}.(17-19)H_2O$, and $Na_2I_8.(10-11)H_2O$, m.p. 16.4°, 2°, and -7° respectively. The first of these phases approximates in composition to sodium diiodoiodate tetrahydrate.

With strongly polar organic solvents, such as nitriles and nitro-compounds of the aromatic series, sodium diiodoiodate forms rather stable addition products which crystallise well and contain two molecules of solvent[151].

Potassium diiodoiodate separates as extremely hygroscopic azure-black (or dark brown) crystals of cubic or prismatic form when a concentrated KI solution containing the stoichiometric amount of iodine is cooled to 0°.[179-183]

Careful study of the potassium iodide–iodine–water system at 0° and 25° by several investigators[155,184-189] has shown that potassium iodide and iodine can react in aqueous solution, forming only two incongruently melting complexes $K[I(I_2)].H_2O$ and $K[I(I_2)_3].H_2O$. Potassium diiodoiodate monohydrate has two modifications[189], m.p. 12.3° and 30°; potassium hexaiodoiodate monohydrate melts at 38°. It has been shown[190] that small quantities of a complex close in composition to potassium octaiodoiodate can form in 5.4 *N* aqueous KI saturated with iodine.

Potassium diiodoiodate was not observed[191,192] in the solid phases which separate in the potassium iodide–iodine–40–60% ethanol (or methanol) systems at 25°.

Potassium diiodoiodate readily forms various addition products with organic solvents. It was found[171,172,176,193,194] that $K[I(I_2)].C_6H_6$, $K[I(I_2)_2].2C_6H_6$, and $K[I(I_2)_4].3C_6H_6$ separate in the solid phase in the potassium iodide–iodine–benzene system at 6–25°.

The formation of stable solvated potassium polyiodoiodates in non-polar benzene is very interesting when it is considered that such solvation is characteristic only for organic solvents with a high dipole moment. Incongruently melting brown-green crystals of $K[I(I_2)].2C_6H_5CN$ separate from benzonitrile containing potassium iodide and iodine[151]. When nitrobenzene, nitromethane, and some other nitro-compounds are saturated with iodine and potassium iodide, a viscous, dark brown liquid is formed, with a constant ratio of these components, corresponding to potassium octaiodoiodate, which could not be isolated[161,195-198].

The ease of formation of potassium diiodoiodate in aqueous and non-aqueous solutions and the difficulty of obtaining it in the absence of a solvent† are linked with the solvation of the cation, which results in an increase in its volume and a decrease in its polarising action on the complex anion[199-201]. With large cations, stable isopolyiodates are formed in the absence of a solvent[173,198,202]. Thus in the $(CH_3)_4NI$–I_2 system the formation of tetramethylammonium octaiodoiodate, m.p. 106.4°, has been shown[173]; it crystallises from benzene as a finely crystalline green-brown powder, which is stable in the air and is not decomposed by water[200,203].

The formation of potassium diiodoiodate in the potassium iodide–iodine system between 75° and 160° and at iodine concentrations of 47–100 mole % has not been established[204-206].

Ammonium diiodoiodate crystallises[181] from aqueous solutions as dark blue crystals, density 3.749 g cm^{-3}, which slowly deliquesce in the air. Studies[208,209] of the ammonium iodide–iodine–water system at 0° and -15° showed the existence of incongruently melting diiodoiodates (anhydrous and trihydrate) and tetraiodoiodate monohydrate, with decomposition temperatures 175.7° and 9.8° respectively. The existence of the octaiodoiodate in nitrobenzene saturated with ammonium iodide and iodine has been demonstrated[171], whereas in benzene, toluene, and benzonitrile at 6–25° complexes other than the unsolvated ammonium diiodoiodate were not observed[151,210].

Rubidium diiodoiodate separates as red-brown rhombs, readily soluble in water, absolute alcohol, and ether[5,146,211-214]. Its solubility[23] in water is 77.5 wt. % at 25° and 84.1 wt. % at 40°.

† The existence of anhydrous and non-solvated potassium diiodoiodate is doubted[199,206,207].

Investigation[173,185,213] of the rubidium iodide–iodine–water system showed the existence of only one anhydrous rubidium diodoiodate, congruently soluble in water at temperatures between 7.8° and 132°.

Hexa- and octa-diodoiodates including four molecules of the solvent have been isolated at 6° from benzene containing rubidium iodide and iodine, but only rubidium diiodoiodate from toluene[24,172,173,176]. In the absence of water or an organic solvent reaction of iodine and RbI was not observed at 60–238°.[205,214]

Caesium diiodoiodate is deposited from aqueous solutions as rhombs or acicular blue-black crystals which become tabular after recrystallisation from absolute alcohol[108,185,211]. Caesium diiodoiodate is stable at room temperature[211]: decomposition with formation of free iodine starts at 115°. $Cs[I(I_2)]$ dissolves incongruently at 25°.[108]

Studies[215,216] of the caesium iodide–iodine–water system at 25° showed that only two[217,218] isopolyiodates can be isolated from aqueous solutions: the diiodoiodate and the polynuclear compound $Cs_2[I_8]$. The individuality of the latter was established not just by chemical and X-ray analyses[76,215] but also by measurement of the rate of loss of iodine from mixtures of caesium iodide and iodine over sodium hydroxide[219].

In studying[176,220] the caesium iodide–iodine–benzene (toluene) systems at 6° and 25°, $Cs[I(I_2)]$ and $Cs_2[I_8]$ were obtained, with heats of dissociation of -17.50 and -15.8° kcal mole^{-1} respectively. Furthermore, a solvate of composition $Cs[I_{9-10}].(1.5–2.0)C_6H_6$, very unstable in air, was isolated from benzene[176,220]; its existence had been mentioned earlier[171,172].

Interesting results have been given[221] about the formation of the compounds $Cs[I(I_2)]$ and $Cs_2[I_8]$ in the caesium iodide–iodine system, which was studied between 60° and 303°.

Yamatera[222] recently suggested the existence of double diiodoiodates of rubidium and caesium: $2Cs[I(I_2)].Rb[I(I_2)]$, $3Cs[I(I_2)].2Rb[I(I_2)]$, and $Cs[I(I_2)].Rb[I(I_2)]$, but they could not be isolated.

Thallium diiodoiodate, isomorphous with $Rb[I(I_2)]$ and $Cs[I(I_2)]$, and tetraiodoiodate are known[30,223,224]. Thallium diiodoiodate separates as black-violet crystals during slow evaporation of a methanol solution of TlI and iodine in a molar ratio between 1 : 1.18 and 1 : 1.30. Its aqueous solutions exhibit the tautomeric equilibrium $Tl[I(I_2)] \rightleftharpoons TlI_3$, which is sharply displaced to the right, owing to the partial oxidation of thallium by iodine and the formation of the stable $[TlI_4]^-$ complex ions in the presence of a large excess of iodine and alkali metal halides: the stability of the alkali metal tetraiodothallates rises from caesium to lithium.

The thallium(I) tetraiodoiodate isolated by Mironov[223] forms light, glistening plates, the colour of iodine, which decompose to TlI and I_2 when heated to 60–100°.

IV. HETEROPOLYHALOGENATES WITH A LINEAR ANION

The common main feature of these compounds is their stereochemical similarity, based on linearity of the complex anion, which consists of three halogen atoms. In the crystals these elongated complex anions are, in the presence of potassium, rubidium, or caesium cations, situated parallel to some plane but at right angles to one another. Therefore the crystals of the heteropolyhalogenates with a linear anion are characterised by high negative double refraction. From the standpoint of the localised electron pair theory[225], the mutual orientation of the chemical bonds in the three-halogen linear anion can be represented on the basis of dsp^3 hybridisation in the form of a trigonal bipyramid with two halogen-ligands at its vertices and with three lone pairs of electrons in the plane of the central section.

Dichloroiodates

The dissolution of iodine monochloride in concentrated hydrochloric acid gave[35,45,143,226–231] a dark brown liquid with 80% $H[ICl_2]$. The instability constant of hydrogen dichloroiodate[230] in perchloric acid at 25° is 6×10^{-3}.

According to recent work[232] solutions of iodine monochloride in hydrochloric acid of various concentrations contain only the complex acid hydrogen hexachloroiodate(V).

Of the alkali metal dichloroiodates, the lithium compound has not yet been obtained and the possibility of obtaining sodium dichloroiodate is doubted[35,143,148,223].

Potassium dichloroiodate[5,37,38,183,234] crystallises as a monohydrate of low stability[234], and the anhydrous compound can be obtained by drying this over magnesium perchlorate[37]. Potassium dichloroiodate was also found to be formed in the KCl–ICl system in nitrobenzene[235,236] and in studying electrical conductivity in the KCl–ICl system[235,237,238]. A thermogravimetric study of this compound showed that it decomposes at 108–110°: the iodine monochloride formed boils off[2]. It has been suggested that a compound of the type $KCl.2ICl$ exists[239].

Crystals of ammonium dichloroiodate are extremely hygroscopic, gradually lose iodine monochloride in air, and are readily soluble in water. There is 87% hydrolysis of ammonium dichloroiodate in its 0.05 N aqueous solution at 25°.[35]

Rubidium dichloroiodate crystallises[5,20,37,143,240] as bright yellow anisotropic hexagonal crystals, whose solubility[241] in water is 54.93 wt.% at 25°.

A study[241] of the rubidium chloride–iodine chloride–water system at 25° showed that the solubility isotherm consists of an RbCl crystallisation branch, of insignificant extent, and the much longer crystallisation branch of the congruently soluble anhydrous rubidium dichloroiodate which is formed in the system.

On heating, rubidium dichloroiodate has been found[241] to be stable up to 136°, above which it decomposes with formation of RbCl and liberation of ICl. The endothermic effect associated with the thermal decomposition of $Rb[ICl_2]$ is at 210°.

Caesium dichloroiodate, according to Wells and Penfield[108], is dimorphous. Crystals of the hexagonal modification separate as hexagons when $Cs[ICl_2]$ is recrystallised from aqueous solutions. The same structure is also observed with caesium dichloroiodate crystals, obtained on passing chlorine into 20% caesium chloride solution containing iodine which has been heated almost to boiling[183,240].

A study[37,88] of the crystal structure of caesium dichloroiodate obtained from aqueous solutions containing various amounts of caesium chloride did not confirm the polymorphism of this compound.

Thorough investigations[242] of the solubility of caesium and rubidium dichloroiodates in hydrochloric acid of various concentrations showed that the solubility curves have minima, at 12.5 M HCl, with concentrations of 2.59 and 10.83 g per 100 ml solution respectively at 0°. In studying the solubility of alkali metal chlorides in iodine monochloride it was found[243] that the golden yellow residues from the evaporation of the filtrate were the dichloroiodates of the corresponding metals. However, the stabilities given[243] for the compounds differ considerably from the results of other authors.

The formation of alkali metal dichloroastatates $M[AtCl_2]$ in solution has been established[244].

Dibromoiodates

The alkali metal dibromoiodates correspond with the acid $H[IBr_2]$, aqueous solutions of which were obtained by Cremer and Duncan[35,143] on dissolving iodine bromide in concentrated hydrobromic acid, as a dark red viscous liquid containing 6% water. The instability constant of hydrogen dibromoiodate(I)[245,246] at 25° is 2.7×10^{-3}–3.3×10^{-3}. Of all the alkali metal dibromoiodates, only the lithium salt has not been obtained, although the possibility of preparing sodium dibromoiodate is doubted[35,148,218].

Potassium dibromoiodate crystallises[5,20,27,29] as the monohydrate, which forms red rhombs, decomposing in air[143,148,183,218,247].

The formation of potassium dibromoiodate was established in physicochemical investigation of the various systems. $KI-Br_2-I_2$ (by electrical conductivity[248]), $KBr-IBr-C_6H_5NO_2$ (by cryoscopy and electrical conductivity[249]), and KBr–IBr.[250]

Thermographic investigation of potassium dibromoiodate showed[2] that partial decomposition of this complex starts at 120°, with a small endothermic effect; complete decomposition takes place at 160°, the iodine bromide formed boiling off.

Potassium dibromoiodate is readily soluble in water (1200 g dissolve in 100 ml water at 18°[27]), decomposes in alcohol and ether, with precipitation of potassium bromide and reacts both with ammonia[251] and with amines, to form addition products of the type $K[IBr_2].2NH_3$, and with ozone and chlorine[148] by the reactions:

$$K[IBr_2] + O_3 \rightarrow KIO_3 + Br_2;$$

and

$$K[IBr_2] + Cl_2 \rightarrow K[ICl_2] + Br_2.$$

These reactions confirm the results of other investigators (see Section II) concerning the coordinating ability of the postively charged iodine central atom.

Ammonium dibromoiodate was obtained as dark red prisms[20,148,218,247]. This compound, unlike the analogous potassium compound, is stable in absolute ethanol, ether, and carbon tetrachloride. Therefore these solvents are sometimes used[143,252] as media for its preparation.

Rubidium and caesium dibromoiodates have been isolated from solutions as red rhombs and prisms[5,21,148,151,218,253,254], which exhibit very low birefringence (the refractive index of $Rb[IBr_2]$ is[255] 1.418). There is a complete analogy between caesium, rubidium, ammonium, and potassium dibromoiodates as regards conditions of preparation and chemical properties[256].

A study of solubility[255] in the rubidium bromide–iodine bromide–water system at 25° showed that iodine and rubidium bromides react to form only one rubidium dibromoiodate, which is anhydrous and congruently soluble. Thermographic and thermogravimetric investigations[255] showed that decomposition, with liberation of iodine bromide, starts at 60° and ends at 238°. The endothermic effect due to this decomposition is at 233°.

The stability of the alkali metal dichloro- and dibromo--iodates in carbon tetrachloride does not correspond with their thermal stability: in carbon tetrachloride at 25° dichloroiodates are more stable[27]. The equilibrium concentration of iodine monochloride in carbon tetrachloride for potassium, ammonium, rubidium, and caesium dichloroiodates is: 2.9×10^{-3}, 5.7×10^{-2}, 3.5×10^{-4}, and $6.0 \times \times 10^{-5}$ M respectively; those of iodine monobromide under the same conditions for potassium, ammonium, rubidium, and caesium dibromoiodates are 4.7×10^{-2}, 8.4×10^{-3}, 1.0×10^{-3}, and 1.4×10^{-4} respectively[27].

Dichlorobromates

Ammonium, rubidium, and caesium dichlorobromates crystallise as bright yellow prisms. They can be made by passing chlorine into hot (50–60°) concentrated aqueous solutions of ammonium, rubidium, and caesium chlorides containing the equivalent amount of bromine[5,20,108,240]. Caesium dichlorobromate can also be made by a "dry method"[143]. Rubidium dichlorobromate decomposes, without melting, at 110°, with evolution of bromine chloride. Caesium dichlorobromate can be recrystallised from aqueous alcoholic solutions, but it breaks down completely in absolute ethanol and ether.

It is suggested[257] that in the dissolution of bromine monochloride in hydrochloric acid the complex acid $H[BrCl_2]$ is formed, with instability constant[117] 0.058 at -1.5°.

Iodochloroiodates

These compounds of the alkali metals and ammonium are derivatives of the acid hydrogen iodochloroiodate, $H[I(ICl)]$, which has not been isolated in the free state. Its instability constant in 0.06–6.5 M HCl is[44,51,117,258,259] 0.6–0.81 at 25° and 0.543 at 3.8°. The instability constants of lithium, sodium, and potassium iodochloroiodates in 0.05–6.0 M aqueous solutions of the chlorides of these metals are[49,51,142,260-263] respectively 0.79, 0.44–0.77, and 0.43–0.67 at 25°.

It is worth mentioning that the values of the instability constants[258,264,265] determined by different authors differ considerably; it is clear that the constant depends not only on the concentration of hydrochloric acid or metal chloride but also on the nature of the extractant used to determine the distribution of iodine between the two phases. Some investigators[240] assume that under these conditions the ions $[I(I_2)_2]^-$ and $[ClI_4]^-$ are formed as well as $[I(ICl)]^-$.

The alkali metal and ammonium iodochloriodates exist only in solutions; attempts to obtain them in the free state have been unsuccessful[5,41,108,260,265-267]. Study of the equilibrium in the potassium chloride–bromine–water system at ordinary temperatures showed that only potassium chloride separates in the solid phase[264,265].

Obviously the polarising action of even a cation as large as caesium is completely sufficient to destroy the coordination of the chlorine and iodine atoms around the iodine central atom. Only tetraethylammonium iodochloroiodate has yet been isolated[116].

Iodobromoiodates

The alkali metal iodobromoiodates can also be considered as derivatives of a complex acid, H[I(IBr)], which Ray[117] succeeded in obtaining at -4° as orange-red crystals (mixed with ice) from concentrated solutions of iodine in 1.5 *N* aqueous hydrobromic acid. At ordinary temperatures this acid is unstable[41,265]; its instability constant at 25° is[258,268] 0.083. It is thought[259,269] that the anion $[I(IBr)]^-$ may be the product of the dissociation of dibromoiodates, by the reaction:

$$2[IBr_2]^- \rightleftharpoons [I(IBr)]^- + [Br(Br_2)]^-.$$

Lithium, sodium, potassium, ammonium, and rubidium iodobromoiodates are unknown in the solid state and the existence of lithium iodobromoiodate even in solution has not been established. The instability constant of sodium iodobromoiodate in 0.9–8.3 *N* aqueous KI at 25° is[126,260,264] 0.069–0.081. In the sodium bromide–iodine–benzene system at 6° the formation of sodium iodobromoiodate was not established[24].

The instability constant[49] of potassium iodobromoiodate in 0.02–8.3 *N* aqueous potassium bromide at 25° is[124,260,262–264] 0.065–0.078.

The formation of complexes was not observed in the potassium (or rubidium) bromide–iodine–benzene systems[24] at 6° or in the potassium bromide–iodine–carbon tetrachloride system[27] at 25°.

Caesium iodobromoiodate is the only alkali metal compound of this type to have been isolated in the free state; it was obtained as reddish-brown rhombs undergoing marked hydrolysis in water and solvolysis in ether[10,108,270].

The study[24,30] of equilibria in the caesium bromide–iodine–benzene (toluene) system at 6° has shown the existence of only one unsolvated caesium iodobromoiodate with a dissociation pressure of 0.00486 mmHg at 6°. According to some results[265] the formation of a compound of the type $CsBr.12I_2$ is possible in a solution containing caesium bromide and iodine.

Bromochlorobromates

It has been shown[55,117,134,271] that the complex acid H[Br(BrCl)] is formed in hydrochloric acid solutions containing bromine; its instability constant[258] is 0.708 at 30°.

Study of the equilibria at -1° in the sodium (potassium) chloride–bromine–water systems has shown that sodium and potassium bromochlorobromates may exist in aqueous solutions, with instability constants of 0.18–0.77 and 0.17–0.91 respectively at 25–30°.[124,134,263] Only the rubidium and caesium bromochlorobromates have been obtained in the free state[42,108].

Bromochloroiodates

This group of anionhalogenates is the most interesting since the complex anion consists of three different halogens. An acid corresponding to these compounds is known, H[I(BrCl)], formed to the extent of 83% acid and 17% water during the dissolution of iodine monobromide in concentrated hydrochloric acid[143]. The instability constant[53,230] of the complex anion at 25° in 0.05–0.09 *N* HCl and in aqueous alcoholic media is 0.022.

Only the ammonium, rubidium, and caesium bromochloroiodates have been obtained from aqueous solutions as individual chemical compounds and described.

A spectrophotometric investigation[53] of the reaction of KCl with iodine monobromide in aqueous alcoholic solutions showed that within the range of component concentrations 0.005–0.5 M potassium bromochloroiodate is not formed, but the complexes 7KCl.3IBr, 3KCl.2IBr, and 2KCl.3IBr.

Ammonium, rubidium, and caesium bromochloroiodates have been isolated as long garnet-red or reddish-orange prisms[5,90,123,272], incongruently soluble in water. They are rather stable when stored in sealed vessels, but in air they gradually lose iodine monobromide and are converted into the chlorides. Rubidium bromochloroiodate decomposes at 231.5° into rubidium chloride and iodine monobromide[9,272]. In aqueous alcoholic solutions containing rubidium chloride and iodine monobromide at concentrations of 0.001–0.01 M, the formation of compounds of the type RbCl.2IBr is possible[53]. The conventional solubility of rubidium and caesium bromochloroiodates in water is 34.7 and 3.7% at 0°, and 56.8 and 6.3% at 20° respectively[272].

When rubidium and caesium bromochloroiodates are recrystallised from aqueous solutions, their molecular compositions change, approaching that of dibromoiodates[13,108]. This behaviour of bromochloroiodates is due to their partial disproportionation by the reaction:

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

and the lower solubility of the dibromoiodates.

Hexafluoroiodates

The hexafluoroiodates can be considered as derivatives of the hexaiodoiodates $M[I(I_2)_3]$, in which fluorine atoms replace iodine atoms. They evidently have a Γ-shaped anion, with a structure similar to that of the $[I(I_2)_3]^-$ ion (see Table 2).

Lithium hexafluoroiodate is unknown and sodium hexafluoroiodate could not be obtained by fluorination of sodium iodide[104,273]. Potassium hexafluoroiodate[14,16,273–266] separates as white crystals in a very low yield on cooling a saturated (97–98°) solution of potassium hydrogen fluoride, fluoride, or nitrate in iodine pentafluoride. Carbon tetrachloride does not affect potassium hexafluoroiodate, but dioxan brings about slight decomposition of it[16]. The compound is stable up to 150–200° above which it gives iodine pentafluoride and potassium fluoride.

The preparation of rubidium and caesium hexafluoroiodates is identical with that of the potassium salt, but here it is possible to isolate other complexes as well[273]: $2RbF.IF_5$ and $Cs[IF_4].IF_5$. The last of these decomposes at 60° into IF_5 and $Cs[IF_4]$. Rubidium hexafluoroiodate can also be obtained by fluorination of rubidium iodide at 100–300° in the absence of hydrogen fluoride[104].

Other Heteropolyhalogenates

Bode and Klesper[104] obtained rubidium hexafluorobromate by fluorinating rubidium bromide with elemental fluorine

above 200°. They did not establish the existence of potassium and sodium hexafluorobromates. Hexafluorochlorates have not been obtained. In the fluorination of rubidium chloride a compound $Rb_3[ClF_6]$ was isolated[104], which later investigators[105] found to be a double salt $2RbF.Rb[ClF_4]$. Alkali metal hexaiodobromates have not been obtained in the free state. From solutions of tetramethylammonium tetraiodobromate in boiling alcohol saturated with iodine, dark green crystals of $[(CH_3)_4N][BrI_6]$, melting at 109°, could be isolated[116,120].

V. HETEROPOLYHALOGENATES WITH A SQUARE PLANAR ANION

The principal common feature of the anionhalogenates described below is the structure of their five-halogen anion (see Section II). Mooney[92] considered that the bonds in this anion must be formed by the combination of the sp^3d^2 orbitals and belong to the octahedral type. Two positions in the octahedron around the atom of iodine (or bromine) are apparently occupied not by atoms but by two lone pairs of electrons of the iodine (or bromine) atom: one above the plane of, for example, the $[ICl_4]^-$ ion and the other below this plane[225]. Hence the structures of the anionhalogenates of this group are reminiscent of the structures of the octahedral complex anions $[TeBr_6]^{2-}$, $[SnCl_6]^{2-}$, $[PbCl_6]^{2-}$, etc. Actually, the I–Cl interatomic distance of 2.34 Å falls within the limits of the Te (or Sn, Pb, Se, Pt)–Cl interatomic distances, which vary between 2.32 and 2.54 Å.

Tetrafluoroiodates

Potassium, rubidium, and caesium tetrafluoroiodates are obtained as white powders which decompose in moist air. The stability of these complexes depends greatly on the size of the cation[105,273]. It has been found that potassium tetrafluoroiodate can be isolated from its solution in IF_5 only at temperatures below 70°, and rubidium tetrafluoroiodate at 70°. Caesium tetrafluoroiodate forms a compound with IF_5 of the type $Cs[IF_4].IF_5$, separating below 60°. When $Cs[IF_4].IF_5$ is heated to 100° in a vacuum, it decomposes with the formation of caesium tetrafluoroiodate. Caesium tetrafluoroiodate separates immediately from its solution in iodine pentafluoride above 120°.

Potassium tetrafluoroiodate slowly decomposes even at room temperature, with loss of iodine; therefore the chemical analysis of this compound gives a low (2–3%) figure for iodine and a high one for fluorine. Rubidium and caesium tetrafluoroiodates are more stable.

Tetrachloroiodates

The alkali metal and ammonium tetrachloroiodates are salts[19,31,143,146,278,279] of the acid hydrogen tetrachloroiodate(III), $H[ICl_4].4H_2O$. This compound, which Caglioti[280] first isolated in the free state, crystallises as orange-yellow hygroscopic plates, not very stable in air. There is 13% hydrolysis of $H[ICl_4].4H_2O$ in its 0.05 *N* aqueous solutions at 25°.[35] In 4–6 *N* hydrochloric acid, ~4.5% of the iodine trichloride present in the form of hydrogen tetrachloroiodate dissociates into iodine chloride and chlorine[281,282].

Hydrogen tetrachloroiodate(III) is the only anionhalogenate acid for which all the alkali metal salts are known.

Lithium tetrachloroiodate is isolated as the tetrahydrate, which forms yellow hygroscopic acicular crystals when chlorine is passed into a suspension of iodine in a concentrated aqueous solution of lithium chloride[146,247,283]. In air, lithium tetrachloroiodate rapidly deliquesces give a yellow liquid.

Sodium tetrachloroiodate[247,283] crystallises as the dihydrate, which is not very stable in air, and forms pale orange rhombs.

Potassium tetrachloroiodate was first obtained as the monohydrate by Filhol[278,279]. It forms golden-yellow crystals[27,143,146,283] which are monoclinic, with lattice parameters[93]: $a = 13.282$, $b = 14.351$, $c = 4.284$ Å, $\beta = 95.72°$, isomorphous with $K[AuCl_4]$.[25] To obtain the anhydrous product the monohydrate was held in a desiccator over phosphorus pentoxide at 4°, or was dried at 40–50° in a stream of chlorine to constant weight[37,38].

The heat of dissociation of the anhydrous potassium tetrachloroiodate in the range 67.5–85° is 29.5 kcal mole^{-1}. The dissociation proceeds in two stages[26,218,247]:

$$K[ICl_4] = K[ICl_2] + Cl_2,$$
$$K[ICl_2] = KCl + ICl,$$

but at 15° iodine trichloride can be isolated[25].

A redox equilibrium is characteristic for solutions of alkali metal tetrachloroiodates:

$$[ICl_4]^- \rightleftharpoons [ICl_2]^- + Cl_2,$$

by virtue of which their concentrated aqueous solutions attack all metals, including gold and platinum, and also react with iodides, with liberation of iodine[35,284]:

$$[ICl_4]^- + 3I^- \rightarrow 2I_2 + 4Cl^-.$$

Ammonium tetrachloroiodate, which crystallises with three molecules of water, has similar properties[25,143,247,278,279].

Spacu and Popea[285] found that the reaction of ammonium tetrachloroiodate trihydrate with ammine complexes leads to the formation of very stable dichloroiodates with a complex cation.

Rubidium and caesium tetrachloroiodates crystallise as anhydrous orange-yellow monoclinic crystals[26,38,143,146,148,247,286,287].

The solubility of rubidium tetrachloroiodate in water at 0° is 7.2%.[283] At room temperature rubidium tetrachloroiodate gradually decomposes with liberation of iodine trichloride. It is noteworthy that Mooney[92] think that rubidium and potassium tetrachloroiodates cannot be isomorphous. A study of the kinetics of the thermal decomposition of caesium tetrachloroiodate showed that the first stage of this process, at 28–116°, is the formation of caesium dichloroiodate, which decomposes at 116–118° into caesium chloride and iodine monochloride (the rate of the first reaction is considerably greater than that of the second). Caesium tetrachloroiodate dissolves slightly in water[146,218].

Tetrabromoiodates

The alkali metal tetrabromoiodates have not yet been obtained in the free state, and are obviously not stable under ordinary conditions[218]. The complex anion $[IBr_4]^-$ exists in hydrobromic acid solutions and has an instability constant of 5.0×10^{-2}.

Trichlorofluoroiodates

Booth and coworkers[274,288] obtained the alkali metal and ammonium trichlorofluoroiodates with the general formula $M[I(Cl_3F)]$ as orange-yellow needles. However, the methods of analysis used by these authors and the fact that they did not determine fluorine directly means that the existence of these compounds at room temperature in the free state has not been substantiated.

Iodotrichloroiodates

Potassium iodotrichloroiodate was obtained as ruby-red crystals below 45° by Cornog and Bauer[239] in studying the KCl–ICl system. The formation of such a complex was confirmed by the same investigators by studying the solubility of potassium chloride in iodine monochloride. However, Fialkov expressed doubt about the possibility of forming the anion $[I(ICl_3)]^-$ in this system[2,238]. It is worth mentioning that solid tetramethylammonium iodotrichloroiodate was obtained over 100 years ago[289].

Tetrafluorobromates

In studying the reaction of isotopic exchange of ^{18}F between HF and BrF_3, Rogers and Katz[290] observed rapid and complete exchange in the liquid phase at 27°. The exchange of fluorine can be explained by the presence in the system of the equilibrium

$$HF + BrF_3 = H^+ + [BrF_4]^-.$$

The formation of the complex anion $[BrF_4]^-$ is also possible as a result of the dissociation of bromine trifluoride[291]:

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-.$$

The solubility of the alkali metal fluorides in bromine trifluoride at 25° increases from lithium fluoride (0.125%) to caesium fluoride (18.8%).[292] The sodium, potassium, rubidium, and caesium fluorides, which are readily soluble in bromine trifluoride, form complexes with it, but the rubidium and caesium tetrafluorobromates were obtained in this way only as solutions in bromine trifluoride[15]. Lithium fluoride does not react with BrF_3 but the chloride reacts with release of elemental chloride and bromine:

$$6LiCl + 2BrF_3 = 6LiF + 3Cl_2 + Br_2.$$

Ammonium fluoride and chloride react with bromine trifluoride explosively. Of all the alkali metal tetrafluorobromates, only the potassium salt has been isolated in a sufficiently pure form; the others usually contain fluorides as impurities, and a sufficiently effective method to remove these has not yet been found. The stability of the tetrafluorobromates corresponds to the sequence[105]: $K[BrF_4] > Na[BrF_4] > Rb[BrF_4] > Cs[BrF_4]$.

Sodium tetrafluorobromate was obtained by reaction of sodium carbonate or fluoride with bromine trifluoride[293]. Heating sodium chloride, bromine, or iodide with bromine trifluoride to 120° and then cooling the solution with liquid air and sucking off the excess of bromine trifluoride leads to the formation of solid phases of variable composition[15] but the fluorination of sodium bromide gives only sodium fluoride in the residue[104,273].

Sodium tetrafluorobromate decomposes rapidly at 80° and does not react (unlike bromine trifluoride) with organic solvents.

Potassium tetrafluorobromate was obtained as a white crystalline powder by recrystallising from bromine trifluoride the product of the reaction of bromine trifluoride with potassium fluoride, chloride, nitrate, chlorate, iodate, or other potassium compounds[15,96,293-296].

When heated, potassium tetrafluorobromate attacks platinum, to give the fluoride and potassium hexafluoroplatinate, and it reacts with potassium bromide and iodide with the violent evolution of bromine and iodine.

Rubidium and caesium tetrafluorobromates are stable only in the presence of an excess of rubidium and caesium fluorides[15,200]. It is possible to obtain these complexes by fluorinating[104,105] rubidium or caesium bromides at 200–250°.

Tetrafluorochlorates.

Study of the infrared spectra of mixtures of hydrogen fluoride and chlorine trifluoride showed that in the $HF–ClF_3$ system the complex $H[ClF_4]$ is formed at low concentrations of the components. The heat of the reaction $HF + ClF_3 = H[ClF_4]$ is 3.92 kcal mole^{-1}.[297] Potassium, rubidium, and caesium tetrafluorochlorates are made[104,105] by the fluorination of the chlorides of these metals at 160–210°. The tetrafluorochlorates are white substances with low melting points (100–200°), and react vigorously with water and alkali metal iodides.

Other tetraheterohalogenates have not been obtained. Only the tetramethylammonium tetraiodochlorate is known[116]; it separates as azure-green crystals from an alcoholic solution when tetramethylammonium chloride and iodine react. Tetramethylammonium tetraiodobromate $[(CH_3)_4N].[BrI_4]$ is also known; it was made by the reaction of tetramethylammonium bromide and iodine in boiling alcohol. On cooling the solution, dark green crystals separated[116], m.p. 124.5°. Caesium and rubidium tetraiodobromates can exist in aqueous solutions[258].

Of the other anionhalogenates which do not belong to any of the classes considered above, we must remember potassium heptafluorochlorate $K_2[ClF_7]$, which was obtained[298] by the action of concentrated hydrofluoric acid on potassium chlorate. However, recent work[16] rejects the possibility of making this compound.

VI. USE OF ANIONHALOGENATES

The chemical properties peculiar to anionhalogenates (ease of thermal decomposition, comparatively low solubility, etc.) were appreciated by even the first investigators of this interesting class of compounds. Thus, first Wells[299] and then Archibald[300] proposed to use the fractional crystallisation of rubidium and caesium dichloroiodates for obtained the pure chlorides. To obtain $Cs[ICl_2]$ Wells dissolved the stoichiometric amounts of caesium nitrate and iodine in hydrochloric acid (1 : 1) at a temperature close to the boiling point of the solution. On cooling, crystals separated; they were recrystallised once or twice from hot acid (1 : 1), then heated to yield pure caesium chloride. Later, Archibald[7] developed the technological production of pure rubidium and caesium compounds free from Li, K, Na, Si, Fe, and Al, based on the use of fractional crystallisation of rubidium and caesium dichloroiodates and dibromobromates. Subsequently Archibald's method was perfected by Ishibashi and coworkers[8], who

found that fourfold recrystallisation of rubidium dichloroiodate gives a spectrographically pure preparation (as regards potassium) even when the initial solution is saturated with potassium. To use this method, rubidium sulphate or any other rubidium salt is dissolved in the minimal quantity of concentrated hydrochloric acid, the stoichiometric quantity of iodine monochloride is added and the mixture cooled to 0°. The precipitate of rubidium dichloroiodate is filtered off, washed with a little cold concentrated hydrochloric acid, dissolved in a little more of this acid containing iodine monochloride, and recrystallised, by adding each time a little iodine monochloride in hydrochloric acid[7,8]. Fractional crystallisation of caesium dichloroiodate was used to obtain pure caesium chloride. After seven recrystallisations a 99.9% product was obtained from 71% caesium chloride[7,8]; this product did not give the spectrographic lines of rubidium. The separation factor of rubidium and caesium[8] when fractional crystallisation is used was 29.1.

Some chemical and physical properties of diiodoiodates were used for the separation of some alkali metals in the presence of others[222]. The possibility of using diiodoiodates for the extractive separation of the alkali metals has also been mentioned[301]. Study[213] of the $RbI-I_2-H_2O$ system showed that the crystallisation of rubidium diiodoiodate is most favourable between 0° and 5° and at a concentration of the components in the solution determined by the section of the isotherm of the crystallisation of this complex, which is adjacent to the $RbI + Rb[I(I_2)]$ eutonic point. On this basis a method of freeing rubidium diiodoiodate from caesium impurity was developed[212,302,303]. After four successive precipitations of rubidium diiodoiodate with the separation of 40% of the rubidium iodide present in the solution, rubidium iodide with 0.02% caesium was obtained from the filtrate — the initial rubidium iodide contained 1.5% caesium. The crystallisation coefficient for this process (Khlopin constant) was 23.4 at 25°.[212,302]

The precipitation of rubidium bromochloroiodate from aqueous solutions was proposed for the preparation of especially pure rubidium chloride, free from potassium impurity[9,11,12,270,271]. It appeared that the coprecipitation of potassium with rubidium bromochloroiodate is very slight; after a single precipitation the concentration of potassium had fallen from 0.5–1.0% to 0.02% or less, and in the precipitation from acetic acid medium the purification factor reaches 300 (from 0.06 to 0.0002%); the factor for purification from lithium is here 15–55 and that for sodium 30–37.[9,272] The precipitate is enriched in caesium when this is present, owing to the lower solubility and greater stability of caesium bromochloroiodate, compared with the rubidium salt.

The precipitation of caesium iodobromoiodate from aqueous alcoholic solutions was recently suggested[10,270] for the preparation of especially pure caesium bromide containing ~0.002% lithium and sodium and 0.005% potassium, and 0.02% rubidium as impurities.

Alkali metal bromides can be separated (with isolation of caesium bromide) by making use of their differing abilities to form stable and readily soluble polybromates[14]. The ease of passing from some anionhalogenates to others without the introduction into technological processes of expensive reagents and the simplicity of thermal decomposition has enabled a complex technological scheme[13] to be worked out for the purification of commercial rubidium chloride with the simultaneous preparation of especially pure caesium salts.

The possibilities of the alkali metal anionhalogenates are, of course, not yet finally exhausted, since the appearance of new representatives of them in the course of the search for new methods of preparation and new interesting properties of the compounds already known cannot be ruled out.

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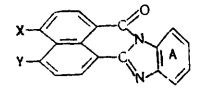
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I. INTRODUCTION

Aroyleneimidazole dyes are usually regarded as forming a separate group of synthetic dyes. They are characterised by the structure



The ring A may be substituted with various groups or fused rings, and positions X and Y may contain hydrogen atoms, various substituents, or another benzimidazole group[1-3].

For obvious reasons this group is also taken to include imides of *ortho*- or *peri*-dicarboxylic and tetracarboxylic acids, as well as compounds, obtained by the interaction of these acids with aromatic *peri*-diamines, which, although they contain no imidazole ring, are very similar to the parent compounds in method of preparation and dyeing properties.

The early aroyleneimidazole dyes were vat dyes. Their brilliance and beauty of shade, great fastness, and comparatively simple manufacture gave the impression that such dyes would displace thioindigoid dyes from the market.

The most important representative of the group of aroyleneimidazole dyes is Indanthren Scarlet GG (Vat