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Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 THE HALOGENS

7.1.1 The Elements

The preparation and use of ^{18}F-labelled inorganic compounds have been reviewed by Winfield.[1] Topol' and Dement'ev[2] have reported SCF-Xα scattered wave calculations for fluorine in its ground and excited electronic states.

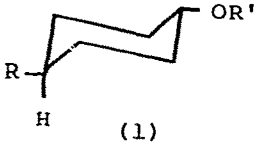
Potential energy models for the interactions in solid chlorine have been re-examined:[3] using isotropic potential functions a partial intermolecular bond is required as well as a molecular quadrupole interaction, but not a dipole term.

Mercury arc photolysis of codeposits of Ar/CH_4 and Ar/F_2 at 15K has produced new i.r. bands which have been ascribed to the $CH_3F...HF$ complex, with H-F and C-F stretches at 3774 and 1003 cm^{-1}, respectively.[4] Warming the matrix to 25K to allow diffusion and reaction (in the dark) gave rise to new absorptions assigned to $H_3C...HF$, ν(H-F) 3764 cm^{-1}. The rate constants of the reaction of F atoms with HBr, Br_2 or O_2 have been calculated from the delayed HF-lasing characteristics.[5] Two reactions and their rate constants are given in equations (1) and (2).

$$F + Br_2 \longrightarrow BrF + Br \; ; \; (1.65 \pm 0.3)10^{-10} cm^3 s^{-1} \qquad ...(1)$$

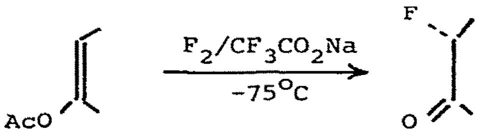
$$F + 2O_2 \longrightarrow FO_2 + O_2 \; ; \; (1 \pm 0.3)10^{-32} cm^6 s^{-1} \qquad ...(2)$$

Rozen et al.[6] have reported selective and efficient (ca. 60%) heterogeneous fluorinations of tertiary C-H bonds by means of dilute F_2 gas at -70°C. Competitive fluorinations of (1)



(1)

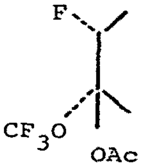
established that the compound with R=t-Bu reacts faster than that with R=Me, thus supporting an ionic electrophilic mechanism. Furthermore, a study of reactions in solution showed that, in non-polar $CFCl_3$, polyfluorinated products are formed rapidly whereas in more polar systems, containing at least 50% $CHCl_3$ which is a good radical scavenger, the reaction is slower and more controlled. Further support for a polar electrophilic substitution mechanism involving F_2 comes from the work of Cacace et al.[7] They investigate the direct fluorination of a representative range of aromatic substrates, e.g. PhH, PhMe, PhF, PhCl, PhBr, $PhNO_2$, PhCN and PhOMe, in inert solvents over the temperature range -154° to +40°C. A mixture of electrophilic fluorinating agents, generated by the action of F_2 on CF_3CO_2Na at -75°C, has been used to convert a variety of enol acetates to the corresponding α-fluoroketones, process (3).[8] The authors claim



...(3)

that the products were obtained in good yield and free of adducts of the type (2) and (3), which are produced when CF_3OF is the

(2)



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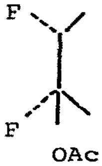


fluorinating agent.

Cartlett and coworkers[9] have established that equilibrium (4) involving elemental fluorine is occurring at room temperature between two of the intercalation compounds formed when pyrolytic graphite reacts with GeF_4 and F_2. The first stage material,

$$C_{12}GeF_5 + \tfrac{1}{2}F_2 \rightleftharpoons C_{12}GeF_6 \qquad \ldots(4)$$

$C_{12}GeF_6$, which loses F_2 in a dynamic vacuum, must be capable of acting as a powerful fluorinating agent.

The effect of traces of water on the kinetics of the reaction between Cl_2 and I_2 in CCl_4 has been studied at 293K;[10] it has been confirmed that water exerts a catalytic effect. The reaction rate (at 298K) was shown to be dependent on the concentration of Cl_2, I_2 and H_2O, all to the first power. The enthalpies of mixing of Br_2 with S_8, EtBr, hexane, hexadecane, or pyridine at 298K, or with I_2 at 323K have been reported:[11] ΔH_f^o for SBr_n, n=0.5, 1, 2 and 4, and ΔH_f^{323} for BrI (-0.52 kcal mol^{-1}) were deduced. The electrical conductivity of X_2, X=Br or I, in both liquid and solid states, containing up to 0.03M halide ion has been measured.[12] In Br_2 the conductivity increases dramatically upon solidification: mixtures of Br_2 with a small amount of $PhNO_2$ have an equivalent conductivity as high as 12 $cm^2 mol^{-1} \Omega$ at -25°C. The $S_2I_4^{2+}$ cation has been prepared for the first time by Passmore et al.[13] The AsF_6^- salt was produced by reaction (5). The structure of the C_2 symmetry cation, Figure 1, approximates to a

$$2I_2 + \tfrac{1}{4}S_8 + 3AsF_5 \xrightarrow{SO_2} S_2I_4(AsF_6)_2 + AsF_3 \qquad \ldots(5)$$

right triangular prism with I-I = 2.597(2)Å, which is intermediate between that distance in I_2(g), 2.662, and in I_2^+, 2.557Å; surprisingly the new dication is not isostructural with P_2I_4. Uruska[14] has determined the stability constants for the formation of I_2 complexes with quinoline and 6-chloroquinoline, in a range of solvents.

The disproportionation of dilute aqueous iodine solutions, between pH 7 and 10, has been reinvestigated by a combination of spectrophotometric and potentiometric methods.[15] The rapid hydrolysis of I_2 to HOI is followed by a slow disproportionation to IO_3^- and I^-. The rate equation (6) was found to describe the rate of disproportionation between pH 7 and 14. The reaction of I_2 with

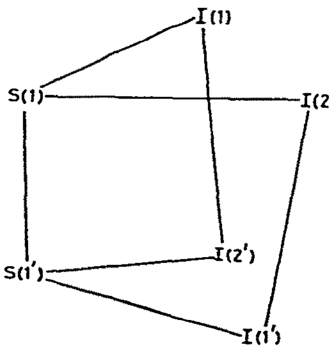


Figure 1. The structure of $S_2I_4^{2+}$, S(1)-S(1') 1.828, S(1)-I(1) 2.858, S(1)-I(2) 3.195, I(1)-I(2') 2.597Å, I(1)-S(1)-I(2) 89.5, S(1')-S(1)-I(2) 92.9, S(1')-S(1)-I(1) 101.6° (reproduced by permission from J. Chem. Soc. Chem. Commun., (1980)289).

$$-d[\Sigma I_2]/dt = (2.5\pm1.6)10^{-2}[HOI]^2 + (1.2\pm0.1)10^{2}[HOI][OI^-] \quad ...(6)$$

aqueous base to generate IO_3^- and I^- has potential value as part of a thermochemical cycle for splitting water, i.e. thermal decomposition of IO_3^- to O_2 and hydrolysis of I^- to HI followed by decomposition to H_2. Mason et al.[16] have examined the reaction between I_2 and hydrated MO, M=Mg, Ca, Sr or Ba. Product separation between insoluble iodate and soluble iodide tends to be incomplete: the best separation was achieved using 5MgO/BaO, which gave the highest yield (76%). Lin[17] has described the chemical forms of radioiodine in the boiling water reactor (BWR) systems: I^- and perhaps HOI are the major species in the reactor water and condensate during normal operation. Following reactor shutdown, IO_3^-, formed by radiation induced oxidation of I^-, dominates. The volatile iodine species, particularly HOI, are believed to be involved in the iodine carryover process, while organic iodides predominate in the off-gas. The variation between 0.2 and 2.5% iodine carryover in the present generation of BWR's is attributed to the effect of coolant impurities, especially Cu^{2+}, on the radiation chemistry of iodine in water.

7.1.2 Halides

The stepwise bond dissociation energies for SF_n have been evaluated on the basis of known heats of formation and from newly determined bond dissociation energies for F_5S-F and F_3S-F.[18] The combined results are depicted in Figure 2, which clearly shows the striking alternation in magnitude.

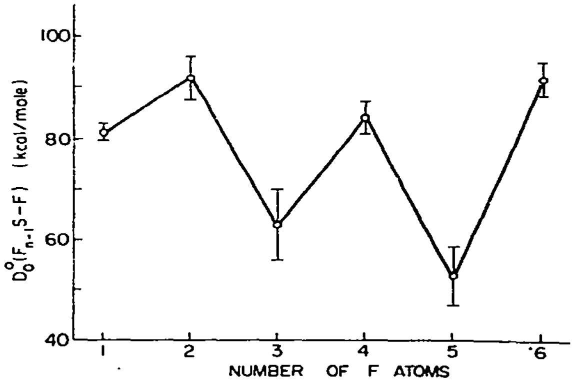
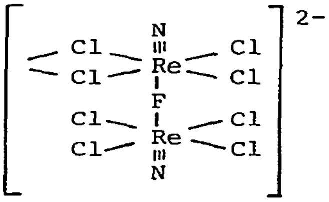


Figure 2. The sulphur fluoride bond dissociation energies as a function of the number of fluorine atoms. (Reproduced by permission from J. Am. Chem. Soc., 102(1980)4024).

The reaction of Ph_4AsF in MeCN with $ReNCl_4$ has yielded $(Ph_4As)_2[Re_2FN_2Cl_7]$:[19] the anion in the new compound is thought to have an essentially dimeric structure (4) for which a strong i.r. band (at 537 cm^{-1}) was assigned to the asymmetric Re-F-Re stretching



(4)

motion. The i.r. and Raman spectra of solutions of Et_4NF in liquid HCl have been obtained and it is proposed that the solvation number of F^- is 4.[20]

Emsley et al.[21] have prepared single crystals of the 1:1 adduct of KF and succinic acid and determined its crystal structure. The fluoride ion lies on a mirror plane and is H-bonded to two carboxylate hydrogens of different succinic acid molecules. Interestingly the F...H and H-O distances are 1.575 and 0.90Å and the FHO angle is 160(2)°, so that the F...O distance is only 2.44Å. Broad line ^{1}H and ^{19}F n.m.r. data have been used to derive structural parameters for $CaF_2.2HF$ and $MF_2.HF$, M=Sr or Ba;[22] the HF_2^- ion is present in all three structures. The products of reaction of dry HNO_3 and the fluorides of Na and Cs have been characterised by Gillard and coworkers.[23] An unstable intermediate from CsF apparently contains the H-bonded $FHONO_2^-$ ion which loses HF readily. The thermodynamic properties of the liquid mixtures $MF-M_2SO_4$, M=Li, Na or K, have been studied by calorimetric and cryoscopic measurements.[24] The enthalpies of mixing are small and mostly negative : poor agreement was reported between 'experimental' partial entropies and those calculated from the Temkin model.

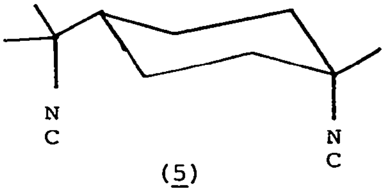
A transient absorbing at about 3400Å (band width ca. 1000Å) was observed after photolysis of aqueous NaCl solutions in the concentration range 5×10^{-4} to 2M.[25] The band was attributed to Cl_2^-. A high pressure mass spectrometric technique has been used to determine the enthalpies of formation of SO_2Cl^- and $(SO_2)_2Cl^-$.[26] The results for the gas phase reactions (7) yield

$$Cl^-.(SO_2)_n \quad + \quad SO_2 \rightleftharpoons Cl^-.(SO_2)_{n+1} \qquad \ldots(7)$$

heats of reaction -21.8 and -12.3 kcal mol^{-1} for n=0 and n=1 respectively. These results are consistent with the estimated values published in 1979 by Robbiani and Franklin.

In the ion exchange chromatographic separation of the chlorine isotopes the role of the eluant has been investigated by Heumann and Baier.[27] The same workers (with Wibmer)[28] have used hydrous ZrO_2 in a column to separate I^-, Br^- and Cl^-; these anions were eluted in that order and an enrichment of the chlorine isotope ($^{35}Cl^-$ is eluted first) was also reported.

Gladfelter and Gray[29] have reported that chloride or bromide ions(X) are complexed in a stable binuclear nickel derivative $[Ni_2X(dmb)_4](PF_6)_3$, where dmb is p-1,8-diisocyanomenthane (5). The dmb ligand bridges the metal atoms in $[Ni_2(CN)_4(dmb)_2]$ (Ni...Ni 4.33Å) and in $[Rh_2(dmb)_4]^{2+}$ (Rh...Rh 4.4-8Å), so that the



(5)

nickel atom in $Ni_2(dmb)_4{}^{4+}$ can be expected to encapsulate ions such as Cl^- or Br^-. Thiocyanate ions also interact with this Ni_2^{4+} entity but the resulting complex is converted to $[Ni_2Cl(dmb)_4]^{3+}$ by the addition of one equivalent of Cl^-.

An iodide ion-selective electrode has been used to measure the rate of oxidation of I^- by $IO_4{}^-$:[30] by contrast with earlier studies no pH dependence was apparent over the range 25 - 35°C.

7.1.3 Interhalogens and Related Species

A study has been made of the kinetics and mechanism of the thermal decomposition of ClF in the range 90°-250°C, 0.3-0.8 atm.[31] The reported activation energies are 8.8±1.0 and 15.2±1.0 kcal mol^{-1} at 90° and 250°C, respectively. Chlorine nitrate, $ClONO_2$, has been produced in a high degree of purity by the single stage reaction of the type shown (8).[32] The yield is highest (92%)

$$M(NO_3)_2 + 2ClF \xrightarrow{< 0^oC} MF_2 + 2ClONO_2 \qquad ...(8)$$

when the anhydrous metal nitrate used is $Pb(NO_3)_2$: lower yields are obtained from the alkaline earth metal nitrates. The synthesis, reaction (9), and characterisation of chlorine trifluoromethanesulphonate has been reported by DesMarteau and coworkers.[33] The product is unstable at 22°C, decomposing

$$CF_3SO_3H + ClF \xrightarrow{-78^oC} CF_3SO_2OCl + HF \qquad ...(9)$$

$$CF_3SO_2OCl \xrightarrow{22^oC} CF_3Cl + SO_3 \qquad ...(10)$$

according to reaction (10). The reactions of the chlorine(I) compound with a variety of perfluoroalkyl halides were described.[34] Perfluoroalkyl esters were formed in reactions of type (11) : disubstituted products were obtained from CF_2Cl_2 (above -50°C),

$$C_2F_5Br + ClOSO_2CF_3 \longrightarrow C_2F_5OSO_2CF_3 + BrCl \qquad ...(11)$$

$$CF_2Cl_2 + 2ClOSO_2CF_3 \longrightarrow CF_2(OSO_2CF_3)_2 + 2Cl_2 \qquad ...(12)$$

equation (12), and from $(CBrF_2)_2$. An S_Ei-type mechanism was proposed for the reactions.

Fluorine atoms, produced by a microwave discharge in NF_3, codeposited with CF_3X, X=Cl, Br or I, in an Ar matrix at 14K are reported to form CF_3XF as a reaction intermediate.[35] On the basis of the i.r. study these new species have a bent C-X-F skeleton; when photolysed with medium pressure Hg arc radiation CF_4 was generated. It was suggested by Jacox that CF_3ClF may be relatively stable.

Chlorine (III) and chlorine(V) fluorides react with $(SiF_3)_2O$ according to equations (13) and (14);[36] with excess $(SiF_3)_2O$ the chlorine(V) intermediate ClO_2F also disproportionates, equation (15).

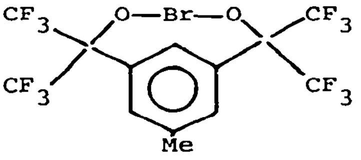
$$8ClF_3 + 10(SiF_3)_2O \longrightarrow 4ClO_2F + 2Cl_2 + O_2 + 20SiF_4 \qquad ...(13)$$

$$ClF_5 + 2(SiF_3)_2O \longrightarrow ClO_2F + 4SiF_4 \qquad ...(14)$$

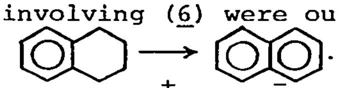
$$12ClF_5 + 26(SiF_3)_2O \longrightarrow 8ClO_3F + 2Cl_2 \; O_2 + 52SiF_4 \qquad ...(15)$$

Waddington and coworkers[37] have prepared both chloro- and bromo-trimethylammonium salts, Me_3NX^+, by a variety of methods (see Chapter 5). Both cations are quite stable in the solid phase as salts of anions such as BF_4^- or SO_3F^-. Haag[38] has demonstrated that N-bromo-N-chloroamines exist and he has prepared and characterised MeNBrCl in CCl_4 solution. Chlorine(I) thiocyanate has been shown to be ClSCN by microwave spectroscopy.[39]

The isolation and characterisation of the first organobrominane (6) has been reported.[40] It is thermally and hydrolytically stable



(6)

at room temperature, sublimes at 60°C in vacuo and melts at 153-4°C. A number of oxidation reactions involving (<u>6</u>) were outlined, e.g. PhSH → PhSSPh, PhNH$_2$ → PhN=NPh, . A simplified synthetic route to the known compounds $Br_2^+Sb_3F_{16}^-$ and $I_2^+Sb_2F_{11}^-$ involves the oxidation of the halogen by $S_2O_6F_2$ followed by solvolysis of the SO_3F^- anion in excess SbF_5.[41] The results of a detailed magnetic and spectroscopic study of materials prepared in this way were also reported. The reaction of excess $BrOSO_2F$ with gold yields $Br_3[Au(SO_3F)_4]$ containing the Br_3^+ cation:[42] this salt will add Br_2 to produce a compound of low thermal stability which apparently contains Br_5^+. Chlorine(I) trifluoromethanesulphonate oxidises Br_2 to form the previously unreported bromine(I) compound.[33] The decomposition of the latter, equation (16), probably proceeds

$$2CF_3SO_2OBr \xrightarrow{22^\circ C} CF_3SO_2OCF_3 + SO_3 + Br_2 \qquad \ldots(16)$$

$$CF_3Br + CF_3SO_2OBr \longrightarrow Br_2 + CF_3SO_2OCF_3 \qquad \ldots(17)$$

via CF_3Br, since reaction (17) was shown to occur.

Passmore et al.[43] have investigated Ruff's observation that the fluorination of AsF_3 by SbF_5 is catalysed by trace quantities of Br_2. They have proposed that BrF, equilibrium (18), is the reactive intermediate responsible for the oxidation. Experimental

$$2SbF_5 + Br_2 \rightleftharpoons 2BrF + SbF_3.SbF_5 \qquad \ldots(18)$$

data have been published for the reaction between gaseous Br_2 and F_2 at pressures in the range 1-200 torr and at 293K.[44] A mechanism involving the intermediates BrF, BrF_2 and BrF_4 was proposed. Miller and Andrews could not demonstrate the formation of BrF as a result of the photolysis of $CHFBr_2$, although IF could be synthesised in this way.[45] The nature of the bonding in the fluorides and oxides of bromine has been investigated by Kirillov and Klimenko[46] with ab initio m.o. calculations.

The bromine(III) cation, $[Br(OSO_2F)_2]^+$, has now been stabilised as its $[Au(SO_3F)_4]^-$ salt:[42] the synthesis involves the oxidation of stoichiometric amounts of Br_2 and Au metal by excess $S_2O_6F_2$. Diarylbromonium salts, which are excellent arylating agents, are now available by the convenient synthetic reaction (19).[47]

Sukhoverkhov et al.[48] have studied BrF_5 and its complexes with

$$2ArH + BrF_3 + 3BF_3 \xrightarrow[CH_2Cl_2]{-70^{\circ}C} Ar_2Br^+BF_4^- + 2HBF_4 \qquad ...(19)$$

SbF_5 by ^{81}Br and Sb n.q.r. spectroscopy.

Bromine(V) fluoride appears to react with uncomplexed MOF_4, M=Mo or W, abstracting oxygen and forming MF_6 and unstable $BrOF_3$ or BrO_2F.[49] On the other hand, Jacob[36] reports that BrF_5 does not react with $(SiF_3)_2O$. Pentafluorophenylbromine(V) tetrafluoride has been prepared in 24% yield by the oxidation of C_6F_5Br with F_2 at 128°C.[50] The ^{19}F n.m.r. spectrum of the C_6F_5 group, the i.r. and mass spectra of $C_6F_5BrF_4$ were reported.

The first example of a positive halogen ion cryptation has been claimed by Pierre et al.[51] The interaction of the cryptand, [2.2.2], $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$, occurs as shown in equation (20) for which the equilibrium constant, $[2.2.2.-I^+][I^-]/[2.2.2][I_2]$, is greater than 10^7. The electrical conductivity and the p.m.r.

$$[2.2.2] + I_2 \rightleftharpoons [2.2.2\text{-}I^+] + I^- \qquad ...(20)$$

spectrum are all consistent with this formulation. The action of an I^+ donating reagent, N-iodosuccinimide, iodine nitrate or I_2, on $[en_2Co(SCH_2CH_2NH_2)]^{2+}$ yields the relatively stable cation $\{[en_2Co(SCH_2CH_2NH_2)]_2I\}^{5+}$, in which the metal-coordinated S atoms are symmetrically linked through the iodine, S-I bond length 2.619(2)Å and SIS angle 173.0(1)°:[52] these parameters are comparable with those in the $[(NH_2)_2CS]_2I^+$ ion.

The simplified synthetic route to $[I_2][Sb_2F_{11}]$ has been mentioned above.[41] In the same publication an unsuccessful attempt to isolate IBr^+ was described : the reaction of $5I_2^+$ and $9Br_2^+$ in $HSO_3F\text{-}SbF_5$ yielded instead IBr_2^+ and an uncharacterised iodine(V) species. Iodine-127 Mössbauer spectra of some polyhalide ions of the type $(X\text{-}I\text{-}Y)^-$ as well as of $[I_2][Sb_2F_{11}]$ and $I(py)_2NO_3$ have been recorded and compared with available data for related compounds.[53]

The interhalogen IF has been generated by the vacuum u.v. photolysis of CHF_2I or $CHFI_2$;[45] it was subsequently trapped in an argon matrix at 12K. A series of 1:1 adducts of ICl with pyridine derivatives has been investigated by molecular spectroscopy.[54] Many adducts were covalent, however when $CHCl_3$ was used as solvent, the 2-methylpyridine, 1,10-phenanthroline and acridine compounds were shown to be ionic.

The interaction of Ph_4PN_3 and IN_3 in CH_2Cl_2 produces $Ph_4P[I(N_3)_2]$.[55] Details of the anion structure could not be completed owing to disorder in the crystal. The first structural determination of a hydrated triiodide salt, $KI_3.H_2O$, has been completed:[56] neutron diffraction was used since the compound shows poor stability to X-rays. The linear anions were found to be nearly symmetrical, with I-I distances 2.925 and 2.935(3)Å.

A strong resonance Raman fundamental, at 113±1 cm^{-1}, together with five overtones, has been reported for I_3^- in a matrix:[57] there are also strong u.v. absorptions at 287 and 355 nm. These results are in excellent agreement with previous solution spectra. The structure of the blue-black iodine complex of amylose (the "linear", helical component of starch) as prepared either from I_2 and I^- in aqueous solution or from crystalline amylose and iodine vapour, has been studied by resonance Raman and ^{129}I Mössbauer spectroscopy.[58] Both materials contain the same major chromophore involving the I_5^- ion. The material produced by the action of I_2 vapour generates I^- either by hydrolysis or by alcoholysis : the hypoiodite also formed in this way was observed in the Mössbauer spectrum.

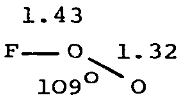
The iodine(III) cation, $[I(OSO_2F)_2]^+$, has been stabilised as its $[Au(SO_3F)_4]^-$ salt.[42] A related compound, $R_fI(OSO_2F)_2$, has been isolated as a product of the reaction of a primary perfluoroalkyl iodide, R_fI, with a halogen(I) fluorosulphate:[59] on the other hand $i\text{-}C_3F_7I$ was converted to $[(i\text{-}C_3F_7)_2I]^+[I(OSO_2F)_4]^-$. Ruppert[60] describes the preparation of aryliodinedifluorides by the direct fluorination of aryl iodides in solution in $CFCl_3$. The iodine(III) compounds precipitate during the course of the reaction and are not readily oxidised further : yields in the range 70-90% were obtained. Naumann and Rüther[61] have prepared a wider range of compounds of this class. They characterised their products more fully and also report that the degree of fluorination to aryliodine(V) compounds can be correlated with the reaction temperature. The direct fluorination of MeI at -110°C in $CFCl_3$ has been described:[62] under these mild conditions the product obtained was CF_3IF_2.

The standard heat of formation of IF_5 has been redetermined as 884.7±1 kJ mol^{-1}.[63] This is in excellent agreement with the results of the earlier studies by Woolf and by Settle et al.. Two new solid-solid phase transitions have been identified by Weulersse et al.[64] from their n.m.r. (^{19}F and ^{127}I) and n.q.r.

(^{127}I) studies on IF_7 over the temperature range 56K to the melting point. This compound does not appear to be affected by $(SiF_3)_2O$ unlike the chlorine fluorides.[36]

7.1.4 Oxides, Oxide Halides and Oxoanions

A new study of the reaction of fluorine atoms with O_2 in an Ar matrix has confirmed and extended the vibrational data on O_2F;[65] the data are consistent with there being an O-O stretching mode in the 1250-1300 cm^{-1} region. SCF-MO calculations for the radical species O_2F and the related thioanalogues, (7)-(10), using the sp basis set, have yielded the geometries shown (distances in Å).[66] The microwave spectrum of fluoroperoxytrifluoromethane, CF_3OOF, has been investigated and ground state structural parameters obtained:[67] O-O and O-F distances, 1.380±0.026 and 1.434±0.018Å respectively. These are in reasonable agreement with the set of data from a recent gas-phase electron diffraction study. The electrochemical production of OF_2 by the electrolysis of HF containing 0 to 20% water has been reinvestigated.[68]



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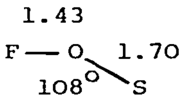

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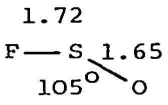

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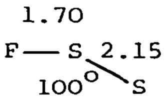


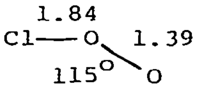
(10)

The reaction of R_fCO_2H, $R_f=CF_3$, C_2F_5, $n-C_3F_7$, or $ClCF_2$, with F_2 in the presence of CsF at -111°C yields the corresponding 1,1-bis(fluoroxy)perhaloalkane in high yield.[69] The fluorination of $(CF_2CO_2H)_2$ forms $[CF_2CF(OF)_2]_2$ but the compound could not be characterised owing to its explosive nature above -20°C. A convenient, two-step method for the introduction of fluorine adjacent to the carbonyl group of ketones, aldehydes, esters and amides has been described.[70] The carbonyl is initially converted to the trimethylsilyl enol ether, which is then treated with CF_3OF at -70°C : since the byproducts of reaction (21) are all gaseous,

$$PhCH{=}C(OEt)OSiMe_3 \xrightarrow{CF_3OF} PhCHFCOOEt + COF_2 + Me_3SiF \qquad ...(21)$$

work-up is straightforward. The decomposition and some reactions of aqueous solutions of the fluoroxysulphate ion, $FOSO_3^-$, have been reported by Thompson and Appleman.[71] Oxygen transfer does not appear to be significant in the oxidations studied, although fluorine transfer is involved in the oxidation of Cr^{2+}_{aq} to CrF^{2+} (ca. 45%) and of $[Co(NH_3)_5ClO_2]^{2+}$ to ClO_2 and $[Co(NH_3)_5F]^{2+}$.

A mixture of Cl_2, O_2 and Ar after passage through a microwave discharge yielded a condensate at 10-22K with the absorption spectrum of ClO.[72] SCF-MO calculations for ClOO,[66] Cl_2O and FClO[73] have been carried out by Hinchcliffe; the optimised geometries, distances in Å, are shown in (11) to (13). The



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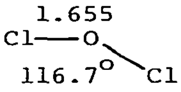

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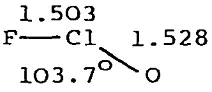


(13)

experimental values for Cl_2O are 1.70±0.02Å and 110.8±1°. The structure of CF_3O_2Cl has been determined from its microwave spectrum:[74] the ground state structural parameters are in reasonable agreement with those obtained by electron diffraction. Asymmetrical $ClO.O_2$ is a possible agent responsible for the effect of O_2 on the quantum yield of the Cl_2-photosensitised O_3 decomposition.[75]

A spectrophotometric study of the kinetics of the reaction between HNO_2 and ClO_2^- has identified both a chloride-catalysed pathway as well as an uncatalysed one.[76] A mechanism involving peroxonitrite and HOCl as intermediates was said to be consistent with the data. The nature of the products of the low temperature reactions between amines and ClO_2 depends on the availability of replaceable protons on carbon or nitrogen atoms.[77] In the absence of such protons a 1:1 adduct is formed.

The electronic spectra of XO_3^-, X=Cl, Br or I, have been investigated by an SCF-Xα study.[78] The results, for valence levels only, for all three species are summarised in Table 1; there are a number of changes in the assignments compared with those made with the help of a minimal basis set.

Emeish[79] has studied the kinetics of the reaction between NO_2^- and ClO_3^- in water and aqueous dioxan. The rate equation (22) applies to both systems; decreasing the dielectric constant

$$\text{Rate} = k[HNO_2][ClO_3^-][H^+] \qquad \ldots(22)$$

Table 1. Ionisation Energies, I_i(eV) for XO_3^-.

	ClO_3^-		BrO_3^-		IO_3^-	
	calc.	obs.	calc.	obs.	calc.	obs.
$1a_2$	10.2	11.2	10.2	11.5	10.1	10.4
$4a_1$	10.3		10.2		10.8	
4e	10.4		10.9		10.3	
3e	10.6		11.0		10.9	
2e	17.7	17.0	15.0	16.4	13.65	14.0
$3a_1$	17.7		15.0		13.65	
$2a_1$	22.1	21.7	22.5	22.4	20.0	19.5
1e	25.3	30.5	28.0	30.6	26.0	28.8
$1a_1$	32.7	34.4	34.5	33.6	28.5	30.0

enhances the rate and is thus consistent with the existence of H_2NClO_5 as the reaction intermediate. Central atom L X-ray emission energies and intensities have been calculated for ClO_4^- by the SCF-Xα scattered wave M.O. method.[80] It was concluded that central atom 3d orbitals make larger contributions to the emission intensities than is indicated by the orbital populations. SCF-Xα calculations of the ionisation energies of ClO_4^-, as well as the isoelectronic SO_4^{2-} and PO_4^{3-}, have been reported.[81] The new data strongly support the original assignments of photoelectron spectroscopy. Christe et al.[82] have used the metathetical reaction (23) to prepare NF_4ClO_4: the new compound

$$NF_4SbF_6 + CsClO_4 \xrightarrow[-78^oC]{HF} NF_4ClO_4 + CsSbF_6 \qquad ...(23)$$

was isolated and characterised but was found to decompose at 25°C to NF_3 and $FOClO_3$.

The bonding in bromine oxides has been investigated by Kirillov and Klimenko[46] using ab initio M.O. calculations. Passage of Br_2, O_2 and Ar through a microwave discharge has yielded[72] a condensate at 10-22K whose absorption spectrum forces a revision of the earlier assignments of the gas phase spectrum for BrO.

Electrolytic oxidation of tetraalkylammonium bromides to the corresponding bromites has been reported:[83] the anodic process is quantitative with approximately 100% current efficiency, the product precipitating from the aqueous solution. Oscillations in the bromide ion concentration during the oxidation of organic substrates by bromate ion in acidic solution have been reviewed by Noyes.[84] He reports that the oscillations in four classes of reaction can all be explained by a generalised mechanism, which is a minor modification of mechanisms reported earlier. In a fifth class of reaction he points out that switching is controlled by the concentration of HOBr rather than Br^-. The perbromate salt of NF_4^+ could not be isolated from the metathetical reaction of type (23);[82] it decomposes in solution to give NF_3, O_2 and $FBrO_2$.

Schmeisser and coworkers[85] have described the use of ozone as an oxidiser for solutions of elemental iodine in strong inorganic acids as a route to the preparation of iodosyl compounds containing IO^+. The production of the sulphate, fluorosulphate and nitrate from the anhydrous acids was reported: from the I_2/O_3 reaction in trifluoroacetic acid a product was isolated and partially characterised which contained iodine in the average oxidation state +4. The absorption and emission spectra of IO in an Ar matrix (10-22K) have been obtained from the condensate after a mixture of MeI, O_2 and Ar had been subjected to a microwave discharge.[72]

The crystal structure of iodylbenzene, $PhIO_2$, has been determined and the expected pyramidal geometry of the primary coordination sphere was confirmed, Figure 2.[86] Interestingly the O(1)IO(2) angle was found to have opened out to 147.8°. Three further I...O

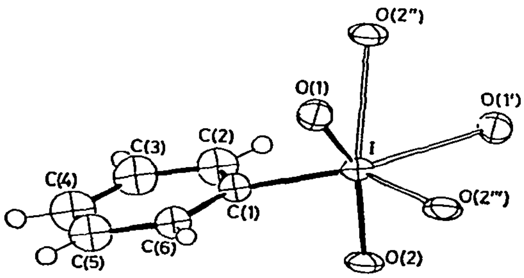


Figure 3. Molecular structure of iodylbenzene (reproduced by permission from J. Chem. Soc. Dalton Trans., (1980)115).

contacts, to O(1'), O(2") and O(2'''), complete the pseudo-octahedral environment of the iodine.

Complex formation between Ag(I) and IO_3^- in equimolar $(K,Na)IO_3$ has been studied by e.m.f. measurements (from 523 to 623K) and solubility measurements (at 553K).[87] The data can be rationalised in terms of a model of stepwise formation of the complexes $AgIO_3$, $Ag(IO_3)_2^-$ and $Ag_2IO_3^+$. Kirilenko and Vinogradov[88] have reported the existence of some water-based glasses containing the IO_3^- ion.

Details of the syntheses of $OI(OTeF_5)_3$ and $I(OTeF_5)_5$ have been published.[89] Evidence from ^{19}F n.m.r. spectroscopy points to the formation of a wide range of compounds in solution of the type $F_xI(OMF_5)_{5-x}$, where M is either Te or Se. However in all instances fluorine occupies the axial position of the square-based pyramidal molecules; hence Seppelt and Lentz point out that both $OTeF_5$ and $OSeF_5$ behave as though these groups are more electronegative than fluorine.

The reactions of iodic and periodic acids with the anhydride of difluorophosphoric acid, equations (24) and (25), produce two new compounds.[90] They are hygroscopic yellow solids, which on the

$$HIO_3 + P_2O_3F_4 \longrightarrow IO_2PO_2F_2 + HPO_2F_2 \qquad \ldots(24)$$

$$H_5IO_6 + 3P_2O_3F_4 \longrightarrow IO_3PO_2F_2 + 5HPO_2F_2 \qquad \ldots(25)$$

basis of their Raman spectra are ionic derivatives containing IO_2^+ and IO_3^+, respectively. The crystal structure of $(IOF_3.IO_2F_3)_2$ at -45^oC has been determined and the tetranuclear unit, Figure 4, consists of two pyramidal IO_3F_2 and two octahedral IO_2F_4 units linked by asymmetric (134^o bent), oxygen bridges.[91] Weaker interactions (not shown) through other oxygen bridges serve to bind the dimers together to form sheets.

The standard enthalpy of formation of crystalline $(IO_2F_3)_2$, di-μ-oxo-bis(trifluorooxoiodine(VII)), has been determined as -984 ± 18 kJ mol^{-1} from measurement of the enthalpy of reaction with excess aqueous acidic iodide solution.[92] The 1:1 adduct between IO_2F_3 and SbF_5 has been investigated by X-ray methods by Edwards and Hana.[93] The compound forms tetranuclear dimers comprising alternate SbF_4O_2 and IF_4O_2 units linked by asymmetric angular oxygen bridges (Sb-O and I-O are 2.05 and 1.80Å). Such a structure points to a contribution from the ionic form $SbF_4^+IO_2F_4^-$

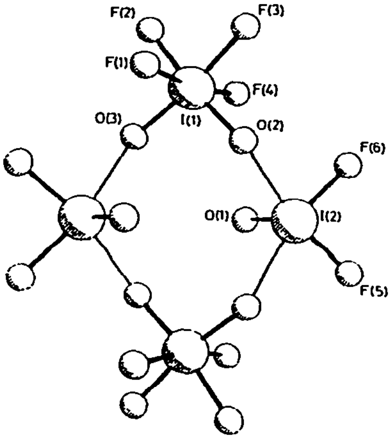


Figure 4. Structure of dimeric $IOF_3.IO_2F_3$ (reproduced by permission from J. Chem. Soc. Dalton Trans., (1980)481).

in which IO_2F_3 is appearing as a stronger F^- acceptor unit than SbF_5.

The reaction of IOF_5 with graphite has been shown by n.m.r. spectroscopy to produce principally graphite-IF_5 compounds.[94] However, there was evidence that some oxygenation of the graphite lattice was also occurring. The ratio IF_5:C in the products of the IOF_5 reaction was found to be larger in some instances than in the products of reaction of IF_5 with graphite. The decomposition process, equation (26), can be rationalised mainly in terms of the

$$IOF_5 \longrightarrow IF_5 + \tfrac{1}{2}O_2 \qquad \ldots(26)$$

formation of gaseous O_2 (ΔH_{dissoc}=494 kJ mol^{-1}) and of IF_5 (ΔH_f^o= -837.3 kJ mol^{-1}), the most stable fluoride of iodine.

The hexamolybdoperiodate anion, $[IMo_6O_{24}]^{5-}$, has been shown by X-ray crystallography[95] to be closely related to $[TeMo_6O_{24}]^{6-}$ and $[CrMo_6O_{24}H_6]^{3-}$: the structure of the iodine(VII)-containing anion, shown in Figure 5, has octahedral coordination of both I and Mo atoms by oxygen. The structure of $[Li(H_2O)_4]_2[Co_4H_{12}I_3O_{24}].3H_2O$ has also been reported:[96] it contains a new type of heteropolyanion in which one Co^{3+} is at the centre of a planar hexagon and three

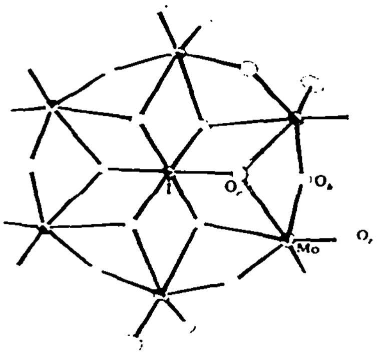


Figure 5. Structure of the $[IMo_6O_{24}]^{5-}$ Anderson-type polyanion viewed perpendicular to the hexagon of the six Mo atoms (reproduced by permission from Acta Cryst., B36(1980) 661).

I(VII) and three Co^{3+} are located peripherally at the corners of the hexagon. The complex anion is related to many hexaheteropolymolybdates and tungstates.

7.1.5 Hydrogen Halides

Microwave spectroscopy is a technique which has proved to be fruitful experimentally for weakly bonded dimers. Millen et al.[97] have observed the rotational spectra of H_2O-HF with a range of isotopic labels. They conclude that the H-bonded hetero-dimer is either planar with C_{2v} symmetry or pyramidal with C_s symmetry, but with a low barrier to inversion at the oxygen. The O...F distance is 2.662Å. The oxetane, $(CH_2)_3O$, hetero-dimer with HF has also been identified and characterised by i.r. and microwave spectroscopy.[98] Hydrogen-bonded π-complexes of acetylene with the three hydrogen halides (not HI) have been characterised in Ar matrices at 15K by i.r. spectroscopy.[99] They were produced either by codeposition of the reagents of by vacuum u.v. photolysis of the vinyl halides : the hydrogen bond strength decreases along the series HF>HCl>HBr. Ethylene was found to be equally as good an acceptor as C_2H_2 towards HF; the H-F stretching vibrations in the complexes were located at 3732(C_2H_2) and 3747(C_2H_4) cm^{-1}.

Giguère and Turrell[100] have presented additional spectroscopic evidence to confirm the predominance of the $H_3O^+F^-$ ion pair in aqueous hydrofluoric acid. They claim that the deuterium analogue is less strongly associated and less extensively ionised. The enthalpies of solution of KF and CsF in the H_2O-HF system have been measured calorimetrically.[101] Both solutes produce a minimum value in ca. 1M aqueous HF : at higher HF concetrations the enthalpy change rises linearly.

The kinetics of the reaction between gaseous HF and solid $CaCl_2$ have been studied in a flow reactor at 293K.[102] The authors concluded that the reaction is first order in the HF concentration. In a subsequent paper the same authors report on the adsorption of HF on CaF_2 at 303 and 333K.[103] They calculated a partial molar absorption enthalpy of -2.98 ± 0.16 kJ mol^{-1} at 303K, a value which is not consistent with the formation of $CaF_2.2HF$. Bonnet and Macherpa[104] have reinvestigated the i.r. spectra of solutions of SbF_5 in HF and have reported some results which are significantly different from those published in 1972 and earlier. They have attempted to analyse the fluoroantimonate absorption region in terms which are compatible with the ^{19}F n.m.r. results of Gillespie and Moss. For the 4000-800 cm^{-1} region they report that H_2F^+ is present when $[SbF_5]\geq50$ mol%; at lower concentrations, down to 20 mol%, they claim that the disolvated proton, $H_3F_2^+$ is dominant. Fabre et al.[105] have carried out an electrochemical study of the oxidation of methylcyclopentane in anhydrous HF and related superacid media.

Hydrogen halide-DMSO phase diagrams have been published:[106] these show that HF forms two solvates, 1 and 4HF, whereas HBr and HCl form incongruent solvates only. There is no evidence for interaction between liquid HCl and Xe at 182K:[107] the calorimetric data yield enthalpies of mixing which agree well with values predicted by perturbation theory.

The He(I) photoelectron spectrum of the "pure" $Me_2O.HCl$ adduct has been obtained by a "stripping" procedure from the spectrum of the mixture.[108] The spectrum was interpreted in terms of an effective transfer of 0.05 electron from the ether to HCl. The identity and geometry of the 1:1 cyclopropane:HCl molecular complex has been determined in the gas phase from its rotational spectrum:[109] the Cl atom is coplanar with the ring and 4.00Å from its centroid. The i.r. spectra of the complexes formed between formaldehyde and

HBr or HCl have been studied in matrices of solid N_2 or Ar.[110] There are significant blue shifts of the C-H stretching fundamental on complex formation.

Proton n.m.r. spectroscopy of aqueous HBr over the concentration and temperature ranges 1-20 mol kg^{-1} and 6-60°C has been treated[111] by the Gutowsky and Saika method. The degree of association was calculated to be 2% at 4 mol kg^{-1}, 11% at 12 mol kg^{-1} and 34% at 20 mol kg^{-1}. Solutions of HBr in sulpholane are brown in colour owing to equilibrium (27). Emsley et al.[112] have measured the

$$C_4H_8SO_2 + 2HBr \rightleftharpoons C_4H_8SO + Br_2 + H_2O \qquad \text{...(27)}$$

equilibrium constant by i.r. and u.v. spectroscopy : the equilibrium constant $K=2.4 \times 10^{-5}$ at 20°C; $\Delta H = -55$ kJ mol^{-1}; $\Delta S = -275 JK^{-1}mol^{-1}$.

7.2 HYDROGEN

Zyryanov et al.[113] have investigated the destruction of H atoms in recombination reactions and in reactions with Cl_2^- radical ions in vitreous solutions of 8M HCl. The activation energies of both processes were found to be 6±1 kcal mol^{-1}. Exchange between gaseous $OH^-(OD^-)$ and $H_2(D_2)$ has been investigated by means of two mass spectrometers and using two modes of ionisation.[114] Exchange of OH^- and D_2 is a relatively slow reaction, collisional frequency 2.9×10^{-2}, and its rate constant exhibits a small negative temperature coefficient, $k = CT^{-0.7}$: the exchange of OD^- with H_2 is 30% slower.

The gas-phase equilibria involving the solvent (S) molecules Me_2SO and Me_2CO have been measured by Kebarle et al.[115]: $\Delta H^o_{n-1,n}$

$$S_{n-1}H^+ + S \rightleftharpoons S_nH^+ \qquad \text{...(28)}$$

and $\Delta S^o_{n-1,n}$ were obtained for n=1 to n=3. The results were compared with previously determined values for $S=H_2O$, Me_2O and MeCN.

A non-spectroscopic method for the analysis of H_2O/D_2O mixtures has been devised:[116] the falling-drop method uses mixtures of bromobenzene and xylene in which a droplet of the water mixture is suspended.

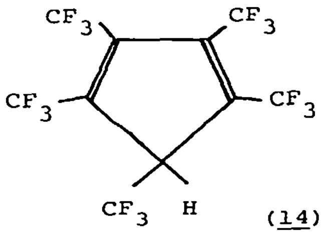
The reactions of the strongly H-bonded anions $CH_3CO_2HF^-$ and $(CH_3CO_2)_2H^-$ with alkyl halides have been followed in the gas phase by ion-cyclotron resonance spectroscopy.[117] The authors point to parallels with synthetically important reactions in glacial acetic acid solutions of alkali metal fluorides.

Ab initio M.O. calculations have been carried out by Jorgensen and Ibrahim[118] to obtain an intermolecular potential function for $(NH_3)_2$. The calculated NN radial distribution functions are in better agreement with X-ray results than are those from molecular dynamics simulations.

Infrared spectra of the probe ion NH_3D^+ in salts with $CuSO_3^-$, SnF_3^-, SiF_6^{2-} and $SnCl_6^{2-}$ provide evidence for symmetrically trifuracated NH...3X hydrogen bonds.[119] Hydrogen bonding between the F of trans-$[OsCl_4FI]^{2-}$ and alkylammonium cations as proton donors are responsible for shifts in the Os←I charge transfer bands.[120] These spectral changes lead to the conclusion that tertiary alkylammonium (e.g. trilaurylammonium) salts exist as "intimate" or "contact" ion pairs in non-polar solvents.

Sheppard and colleagues[121] have reported the i.r. absorption frequencies corresponding to the vibrations of μ_3-bridging hydride ligands in a number of metal hydride cluster compounds; they have developed a vibrational model which leads to a simple relationship between the M-H stretching frequency and the M_3H geometry. It is claimed that this model is equally applicable to the study of hydrogen atoms absorbed on metal surfaces. Knop et al.[122] have sought further support for their views that: (i) the stretching frequency of highly bent H-bonds decreases with increasing temperature, regardless of whether the bonds are static or dynamic in character or to a single or to several acceptors, and (ii) departures from symmetrical tri- or bi-furcation towards asymmetric situations lower the stretching frequency.

Laganis and Lemal have succeeded in synthesising 5-H-perfluoropentamethylcyclopentadiene, (14);[123] this a volatile liquid which



(14)

attacks even silylated glass. It is freely soluble in water in which it ionises to $C_5(CF_3)_5^-$, the pK_a of which process was estimated to be $\leqslant -2$. Hino and Arata[124] have synthesised a solid superacid with $H_o \leqslant -16.04$, the strongest surface acid system yet reported, and which can be used at temperatures up to 650°C. The material was prepared by exposing $Zr(OH)_4$ to 0.5M H_2SO_4 and then calcining in air at 575-650°C. Pressed pellets of the new layer compound $[Zn_2Cr(OH)_6]OH.nH_2O$ have been shown to possess a high proton conductivity;[125] Lal and Howe attribute this to facile proton transfer between H_2O and OH^-.

The electrical conductivities of some solutions in trifluoromethanesulphonic acid have been determined by Russell and Senior.[126] The $CF_3SO_3^-$ ion appears to possess an abnormally high mobility and a proton-jump mechanism was inferred. Sulphuric acid behaves as a weak electrolyte and SO_3 is a non-electrolyte : KNO_3 and KH_2PO_4 appear to generate NO_2^+ and the phosphate acidium ion, $P(OH)_4^+$, respectively. Infrared spectroscopy has been used in a new study of aqueous protonic acids having $pK_a < 1$:[127] the results were discussed in terms of the readily polarisable H-bonds, $AH...OH_2 \rightleftharpoons A^-..H^+OH_2$, being responsible for part of the continuous absorption spectrum. The position of water bands in more dilute solutions can be used to characterise the acceptor strength of the anion. Symons[128] has pointed out that the conclusion,from spectroscopic evidence, that H_3O^+ is "practically" planar is dubious : he has reinterpreted the data and has arrived at a value, 111°, for the HOH angle which is close to that found by diffraction studies on the ion in the solid state.

The trihydrate of pyridine, previously thought to be the dihydrate, has now been characterised.[129] It consists of layers of water molecules H-bonded to form 4-, 5- and 6-membered rings, in the ratio 1:2:1, which are H-bonded to pyridine molecules, O-(H)..N = 2.796Å. Each hydridic hydrogen in $(NaHBMe_3)_4.Et_2O$ is four coordinate being surrounded by three sodium atoms as well as by a boron atom.[130]

An extremely short O-H...O, 2.382(6)Å, bond has been identified in the structure of $K_3[Pt\{(SO_3)_2H\}Cl_2]$ and this H-bond links the sulphito ligands.[131] The crystal structures of potassium hydrogen difluoromaleate (KHDFM) and potassium hydrogen difluorofumarate (KHDFF) have been determined by single crystal X-ray methods.[132] The HDFM anion has a closed ring structure with a short intramolecular H-bond, 2.415(1)Å : the HDFF ions form infinite chains via similarly short H-bonds 2.450(5)Å. X-ray studies on salts of $RhCl_4^-$ containing sulphoxide ligands have revealed the existence of the H-bonded cation $[Me_2SO..H..OSMe_2]^+$ with an O..H..O distance of 2.42Å.[133]

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