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Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 THE HALOGENS

7.1.1 The Elements

Reviews have appeared of industrial fluorine chemistry[1] and of methods of fluorination in organic chemistry.[2] Elemental fluorine cleaves the Sn-C bond in aryl tin compounds at or below 0°C in solution in inert solvents to form aryl fluorides.[3] It was claimed that the reaction is a rather general method for aromatic fluorination and the method was used to generate labelled fluorobenzene, starting with $^{18}F_2$. Direct fluorination of alkoxy- or phenoxy-phosphines in dilute solution in $CFCl_3$ with elemental fluorine at -78°C has been shown to yield the expected phosphorus(V) products.[4] A gas phase chemiluminescence has been observed during the etching of silicon by gaseous F_2; both processes exhibit the same activation energy.[5] From the observed temperature and pressure dependencies it was concluded that the primary etch product is SiF_2 and it is this that is involved in the chemiluminescence reaction with F_2.

Adcock and coworkers[6] have described what they call a new concept in direct fluorination methodology as well as an apparatus designed to achieve conditions for the rapid and continuous fluorination of

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hydrocarbon molecules under controlled conditions of temperature and concentration. Results from the fluorination of neopentane were reported which imply significant deviations from the statistically calculated ratios of specific isomers. Thus of the two heptafluoroneopentane isomers expected to dominate (41% each) in the mixture of products only one $C(CH_2F)(CHF_2)_3$ was obtained and in 100% yield. The apparent order of hydrogen reactivity is $CH_3 > CH_2F > CHF_2 >> CF_3$. Further information has also appeared on the behaviour of acetyl hypofluorite, MeCO(OF), as generated by the action of F_2 gas on a suspension of NaF, NaO_2CMe or NaO_2CCF_3 in acetic acid:$CFCl_3$ (1:9) at -78°C.[7] Not only is F_2 virtually insoluble in acetic acid but it is also unreactive towards it under these conditions. The hypofluorite formed at -78°C can be kept at room temperature for a short time with no appreciable loss of oxidising power, as shown by its syn addition to trans stilbene.

Cartwright and Woolf[8] have discussed the halogenating abilities of the couples E_3AX_2/E_3A, where A is a main group (V)-(VIII) element, X = Cl or F, and E is a bonded group (e.g. Ph) or non-bonded electron pair. Based on the available experimental data (Table 1) they deduce a reactivity sequence for X = F of
$Kr > Xe \sim Cl > Br > I > S > Se > Te \sim As \sim Sb > P$.

Table 1. Enthalpy differences[8] ($H_f^o(E_3AF_2)-H_f^o(E_3A)$) in the fluorinating couples E_3AF_2/E_3A/kJ mol^{-1}.

Group V		Group VI	Group VII	Group VIII
PF_5/PF_3 -621	$Ph_3PF_2(s)/Ph_3P(s)$ -601	$SF_4/S(s)$ -391	ClF_3/ClF -101	
AsF_5/AsF_3 -409	$Ph_3AsF_2(s)/Ph_3As(s)$ -490	$SeF_4/Se(s)$ -401	BrF_3/BrF -182	KrF_2/Kr +60
SbF_5/SbF_3 -494	$Ph_3SbF_2(s)/Ph_3Sb(s)$ -487	$TeF_4/Te(s)$ -486	IF_3/IF -373	XeF_2/Xe -107

The kinetics of reactions (1) and (2) at room temperature as well

$$Cl + ClNO \rightarrow Cl_2 + NO \qquad ...(1)$$

$$Cl + ClNO_2 \rightarrow Cl_2 + NO_2 \qquad ...(2)$$

as the photochemistry of $ClNO_2$ have been studied by Nelson and Johnston.[9] The dominant photodissociation process at 350nm for $ClNO_2$ was shown to give $Cl + NO_2$. The reaction of Cl atoms with ozone in an Ar gas stream has been shown to produce ClO radicals which were characterised vibrationally with the help of four isotopically substituted species.[10] Both ClOO and ClClO were also detected but there was no sign of asymmetric ClO_3 species. Photolysis of Cl_2/O_3 mixtures ($\lambda > 330nm$) in an Ar matrix at 10K generates a number of chlorine oxide species:[11] ClClO absorptions in the i.r. spectrum appeared first, then ClO dimer bands; after 5h the ClOO species was observed. Under the same conditions no chlorine oxides were detected during the photolysis of Cl_2/O_2 mixtures.

A procedure for the synthesis and isolation of ^{77}Br for nuclear medicine research has been developed.[12] Metallic Mo targets were irradiated with medium energy protons at high beam currents. Following workup ^{77}Br was recovered with a 91±7% chemical yield accompanied by low levels of two other radioactive species, ^{76}Br and ^{82}Br. The rate of the acid-catalysed bromination of 2,4,6-trimethylacetophenone is first order in Br_2 in 50% aqueous acetic acid.[13] This contrasts with the behaviour of acetophenone and other ketones under comparable conditions. The likely mechanism for this unexpectedly rapid bromination of the hindered ketone was discussed.

The equilibrium partition coefficients of iodine species between water and the gaseous phase have been measured at 21° and 72°C as a function of the concentration of iodine.[14] When the total aqueous phase iodine concentration exceeded $10mgl^{-1}$ the dominant species is molecular iodine : at lower concentrations convincing evidence was produced by chemical analysis of both phases that HIO is also present in both phases. The partition coefficient data were used to estimate the equilibrium constant for (3) and some thermodynamic properties of HOI.

$$I_2 + H_2O \rightleftharpoons HI + HOI \qquad \ldots(3)$$

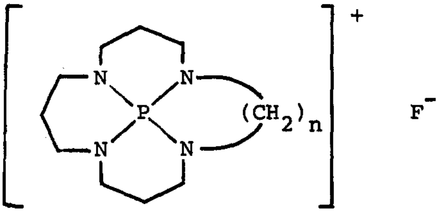
Resonance Raman spectra of I_2 ($\nu = 209cm^{-1}$) dissolved in $AlCl_3$-NaCl (63-37 and 50-50 mol%) melts have been obtained;[15] I_2^+ has been similarly investigated in the more acidic melt. The complexes of I_2 with (a) the π donors, naphthalene, biphenyl and hexamethylbenzene, and (b) the n donors, aniline and o-toluidine have been investigated in CCl_4 by the constant activity method (sometimes known as the polyiodide solubility method).[16] The association constants and heats of formation of the complexes were determined and compared with the data obtained using conventional spectroscopic methods. Other workers have investigated I_2-arene complexes in heptane to look for the correlation predicted by Mulliken between oscillator strengths and the heats of complex formation.[17] After correcting for I_2-heptane interactions a satisfactory correlation was confirmed even for these weak complexes.

7.1.2 Halides

Hoppe[18] has reviewed the progress in the chemistry of fluoride complexes of the transition metals (especially of the first row). As is to be expected his account is authoritative and inspiring. Intermolecular F---F contacts in 15 crystal structures have been analysed and the van der Waals radius of the covalently bound fluorine atom confirmed at 1.40Å.[19] An analogous approach to the intermolecular contacts between pairs of the heavier halogen atoms was shown to be unsuitable as a basis for determining their radii.

The final product of the fluorination of $Re(CO)_5Br$ by AgF has been identified as $[Re(CO)_3F]_4.4H_2O$:[20] it appears to have been formed via $Re(CO)_5F$ although the origin of the water in the structure was not discussed. The structure is interesting in that $Re(CO)_3$ and μ_3-F units form a cubane-like cluster. The water molecules H-bond to F and to each other (O(H)---F, 2.84, and O(H)---O, 2.99Å). Fluorine bridges are also found in the crystal structures of $MF_4O.SbF_5$, M = Mo or Re, where they are formed in preference to oxygen bridges.[21]

A new source of naked fluoride ion has been identified by Richman and Flay:[22] these workers noticed that the hygroscopic solids (1), n = 2 or 3, behave as ionic species in MeCN, i.e.



(1)

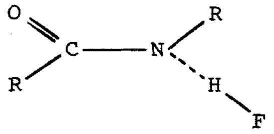
no P-F n.m.r. coupling constant, ^{31}P shifts identical for analogous F^- and Cl^- salts, fluorinate $PhCH_2Br$ a hundred times faster than KF/18-crown-6 in MeCN. The analogous compounds with $n \geqslant 4$ bridges behave differently and are significantly more volatile. The standard free energies of transfer of KF from water to aqueous mixtures of DMSO, DMF, MeCN, 1,2-dimethoxyethane(DME) and 2-methoxyethane(ME) have been determined at 25°C electrochemically.[23] The results show the trend for fixed

DME > DMSO $\geqslant$ DMF >> MeCN $\sim$ ME

concentrations of water.

Boyer et al.[24] have reported that $(EtO)_3SiH$ and $Me(EtO)_2SiH$, activated by KF or CsF, are efficient and selective agents for the heterogeneous reduction of carbonyl groups. The same workers have also reported that CsF in the presence of $Si(OR)_4$ catalyses the Michael addition of monoketones.

Ab initio LCAO-MO-SCF calculations have been performed on the most likely interactions between F^- and H_3BO_3:[25] these show that $BF(OH)_3^-$ is the most stable product but by only 33kJ mol^{-1} relative to the H-bonded product F^----$HOB(OH)_2$. Nevertheless the results of ^{19}F and ^{11}B n.m.r. spectra (solutions) as well as i.r. spectroscopic studies (of the solid phase) are consistent with the hydrogen bonded product. A 1:1 adduct of KF and uracil has been prepared;[26] its i.r. spectrum reveals the presence of an asymmetric N-H---F^- interaction. Clark et al.[27] have reported evidence for the formation of strong H-bonds in solutions of the (heavier) alkali metal fluorides in a number of aliphatic diols. Deuteration of $KF(CH_2CO_2H)_2$ has no effect on the bond lengths in the adduct.[28] The only significant isotope effect is in the bond angle at F^- which increases by 12.5° from 116°. Ab initio LCAO-MO-SCF calculations have been performed on the formamide-, acetamide-, methylformamide-F^- complexes to obtain estimates of the H-bond energies with respect to amido anion and HF.[29] The optimised geometry for all three species (2) has the carbonyl



R = H or Me

(2)

group trans to the H-bonded fluorine. Experimental data were also reported including a crystalline solvate $KF.3HCONH_2$, i.r. ^1H and ^{19}F n.m.r. spectroscopic studies. The authors go on to draw attention to the biological effects that are being linked to fluorides and suggest that H-bonding of F^- to sites on peptides could offer an explanation of some of these.

The kinetics of oxidation of aqueous Br^- by ozone according to equation (4) has been measured spectroscopically.[30]

$$Br^- + O_3 \longrightarrow BrO^- + O_2 \qquad \ldots(4)$$

7.1.3 Interhalogens and Related Species

Solutions of osmium(VI) fluoride in liquid Cl_2 are strongly coloured (blue/violet) however the reagents can be separated almost quantitatively afterwards.[31] The analogous reaction with bromine is irreversible and produces $Br_2^+OsF_6^-$.

A single crystal study of Ph_4AsCl_3 is the first known X-ray determination of a compound containing the Cl_3^- ion.[32] The latter is almost linear, angle 177.5(2)°, and is asymmetric, Cl---Cl distances 2.227(4) and 2.305(3)Å.

Pentafluorophenylchlorine difluoride has been prepared by the oxidation of C_6F_5Cl at 117°C with F_2.[33] The liquid product (b.p. 97°C) shows a ^{19}F n.m.r. spectrum at 25°C with the equivalent fluorines on Cl coupling (19Hz) to the two ortho fluorines. The 1:1 adduct of ClF_3 with BiF_5 has been investigated by ^{209}Bi and ^{35}Cl n.q.r. spectroscopy.[34] The data are said to be consistent with the presence of trans fluorine-bridged BiF_6 units. The optimum conditions for the synthesis of ClF_5 from ClF_3 and F_2 have been determined by Slivnik et al.[35] Nickel(II) fluoride was shown to have a favourable catalytic effect on the reaction. The preferred temperature is 250°C since at 300°C the reaction although faster does not go to completion.

Bromine is oxidised by OsF_6 to form $Br_2^+OsF_6^-$;[31] the new compound is only the second Br_2^+ salt to have been isolated. Diarylbromonium compounds have been prepared efficiently in CH_2Cl_2 by reaction (5).[36a] The addition of MeCN helps to

$$2HgAr_2 + BrF_3 \longrightarrow Ar_2Br^+F^- + 2ArHgF \qquad \ldots(5)$$

suppress the formation of secondary oxidation products, whilst

BF_3-etherate accelerates the reaction. When diarylmercury is replaced by $SnAr_4$ reaction (6) takes place and the bromonium

$$SnAr_4 + BrF_3 \xrightarrow{BF_3.Et_2O} Ar_2Br^+BF_4^- + Ar_2SnF_2 \qquad ...(6)$$

product is more readily produced. The thermodynamics of process (7) have been determined spectrophotometrically[37] in 50% (v/v)

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad ...(7)$$

acetic acid over the temperature range 24 to 46°C.

Pentafluorophenylbromine(III) fluoride has been prepared by the oxidation of C_6F_5Br with F_2 at 128°C;[38] the new compound was characterised by ^{19}F n.m.r., i.r. and mass spectrometry. Perfluoro-n-propylbromine(V) fluoride has been prepared by the fluorination of n-C_3F_7Br at 0°C with F_2.[39] This new compound is a liquid which decomposes slowly at 0°C but is stable indefinitely under helium at -30°C. It was characterised by analysis, i.r. and ^{19}F n.m.r. spectroscopy : the latter technique implied that all fluorines on Br are equivalent and in a similar environment to the four equatorial fluorines in BrF_5.

The crystallisation of $[Sb(S_2CNEt_2)_2I]$ from CH_2Cl_2 in the presence of molecular iodine has yielded crimson crystals of $[Sb(S_2CNEt_2)_2I].(0.5I_2)_x$ where $x \leqslant 1$.[40] The crystal structures of two samples having x = 0.56 and 0.84 show a decrease in cell volume with increasing I_2 content : this is due to polymer strands of composition $[Sb(S_2CNEt_2)_2I]$ being linked with increasing efficiency to one another by iodine molecules (I-I, 2.78 and 2.75Å respectively), the contact atoms in each strand being the iodine on antimony, see Figure 1.

This arrangement approximates to that reported[41] for (2,6-diacetylpyridinedihydrazone)diiodocopper(II).½I_2 which contains an essentially linear centrosymmetric I_4^{2-}: in this an I_2 molecule (2.806Å) serves to bridge two I^- ions (3.35Å). Sharp and coworkers[42] have reported that molecular I_2 is oxidised by PF_5 in IF_5 at room temperature giving $I_2^+PF_6^-$ and PF_3 : I_2^+ is also formed as an initial product when UF_6 is the oxidant. Although several solids containing the I_3^+ cation are known the non-linear structure of the cation has been inferred from Raman and n.q.r. spectroscopy alone. Passmore et al.[43] have

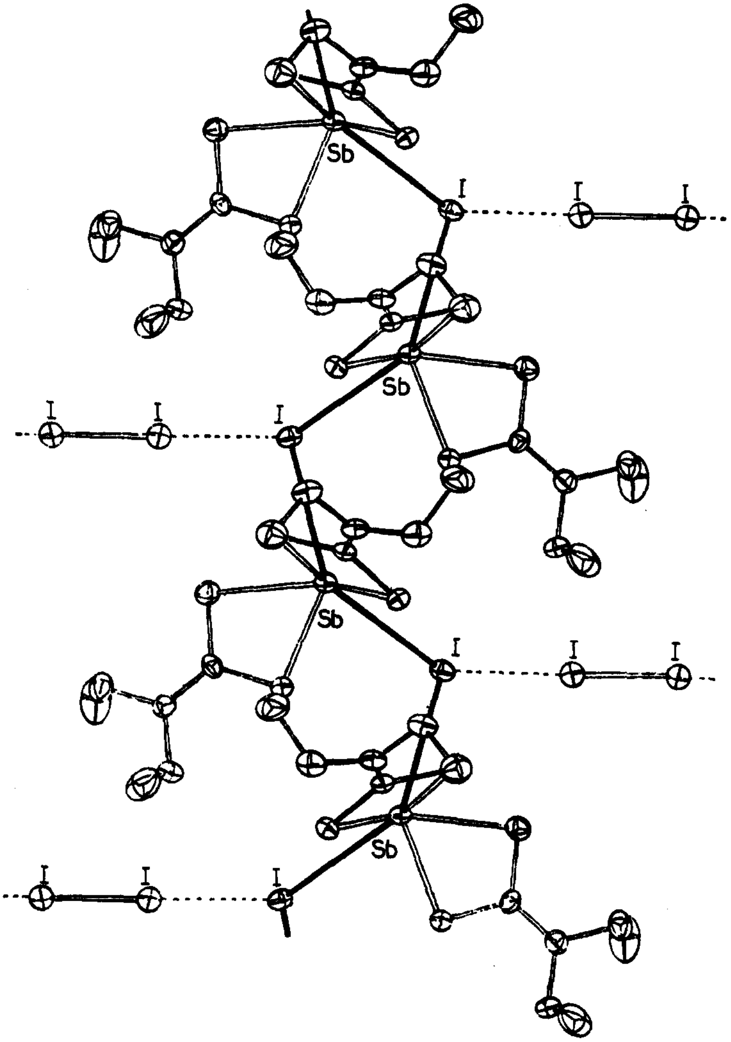
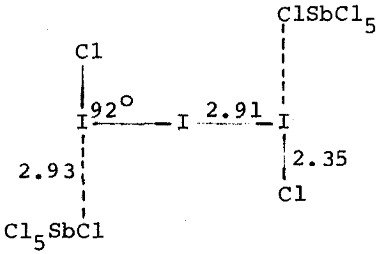


Figure 1. A single polymeric strand of $[Sb(S_2CNEt_2)_2I].0.5I_2$ showing the bridging iodine atoms interacting with iodine lattice molecules (reproduced by permission from J. Chem. Soc. Dalton, (1981)1360).

successfully solved the crystal structure of I_3AsF_6 for which the I-I bonded distances are 2.660 and 2.669(2)Å with the angle 101.75(6)° : interionic I---F distances range from 2.73 to 3.35Å.

The crystal structure of $MgI_8.6H_2O$ has been determined from neutron diffraction data.[44] The I_8^{2-} anions can be considered as two asymmetric I_3^- units linked by an I_2 to form a Z-shaped ion, similar to that found in Cs_2I_8. Interanion interactions (I---I, 3.84Å) in the magnesium salt are responsible for the black lustre of the crystals. The structure of $CaI_{10}.7H_2O$ has been investigated by the same workers.[45] It comprises two I_5^- anions, each approximately L-shaped, as well as the novel $Ca(H_2O)_7^{2+}$ ion. Thomas's study[46] of the phase diagram of the ternary system MgI_2-I_2-H_2O at 0°C has revealed that only one polyiodide exists, $MgI_{11}.9H_2O$; between 0°C and room temperature this phase decomposes to $MgI_8.6H_2O$.

Ruff's adduct, $SbCl_5.3ICl$, has been re-examined by Pohl and Saak[47] and Thorup and Shamir.[48] Both groups have determined the crystal structure of this phase whose composition was originally thought to be $I_2Cl^+SbCl_6^-$ on the basis of Raman studies. The cation is in fact $I_3Cl_2^+$ and its dimensions, and those of $I_3Br_2^+$ in $SbCl_5.ICl.2IBr$, are shown in (3) and (4), bond lengths in Å as



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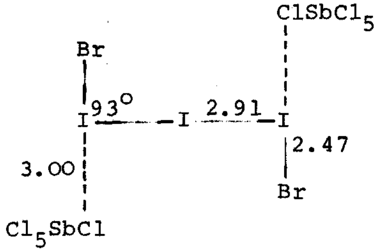


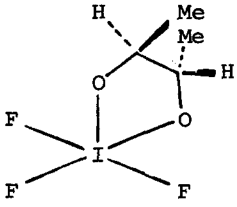
(4)

determined at 143K by Pohl and Saak.[47] Thorup and Shamir have accordingly reassigned the Raman spectrum of $I_3Cl_2^+SbCl_6^-$.[48]

The salt $[N(PPh_3)_2][I(SCN)_2]$ has been prepared by the oxidation of $[N(PPh_3)_2]I$ with thiocyanogen.[49] The i.r. and Raman spectra of the anion imply a near-linear I-I-S arrangement. Although the related salt containing the $I_2(SCN)^-$ ion could not be prepared in a pure state its vibrational spectra are consistent with an I-I-S skeleton. From the reaction with selenocyanogen the compound containing the $I(SeCN)_2^-$ was prepared for the first time.

All three isomeric aminopyridinium salts of ICl_2^- and IBr_2^- have been studied by i.r. and Raman spectroscopy.[50] Sasaki et al. concluded that both symmetric and asymmetric forms of the anions exist in the solid state and for ICl_2^- in MeOH solution, however IBr_2^- is asymmetric in MeOH. Huong and Cruege[51] have recorded the resonance Raman spectrum of IBr in a range of solvents.

The crystal structure of $ICl_2^+SbF_6^-$ is of interest in that the ICl_2^+ ion interacts with the anions through very short fluorine bridges, I---F, 2.650(6)Å, thus leading to rectangular geometry about the iodine(III) atoms.[52] In the condensation reaction of IF_5 with ethyleneglycol $IF_3(OCH_2CH_2O)$ is formed with the loss of two HF molecules : this ^{1}H and ^{19}F n.m.r. study has shown that 2,3-butanediol behaves in a chemically similar manner,[53] however of the two diastereoisomeric products, (5) and (6), one predominates over the other in the reaction mixture. Iodine(V) fluoride vapour (0.4 torr) treatment of polyacetylene film causes the electrical conductivity to increase markedly up to $150\Omega^{-1}cm^{-1}$;[54] this conductivity decreases gradually when the doped film is stored in a vacuum. The reaction of IF_5 with elemental sulphur, reaction (8), has been used to prepare SF_4 on a millimolar scale.[55]



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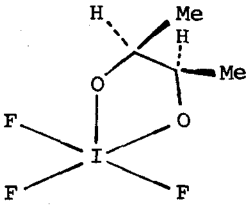


(6)

$$4IF_5 \ + \ 5S \longrightarrow 5SF_4 \ + \ 2I_2 \qquad \ldots(8)$$

7.1.4 Oxides, Oxide Halides and Oxoanions

The i.r. spectrum of HOF at -195°C contains absorptions assignable to intermolecular bonds;[56] the spectrum could be interpreted in terms of a simple cyclic dimer although alternative polymeric structures cannot be excluded. A preliminary report of the first example of an iodine hypofluorite appeared in 1979; a thorough characterisation of $FOIF_4O$ has now been published by Christe et al.[57] The reaction of NO with OF, to form NO_2 and F, has been studied at 298K by the discharge flow/mass spectrometric technique.[58]

The enthalpy of reaction of $CsSO_3(OF)$ with aqueous HI has been measured by solution calorimetry and the $\Delta H_f^{\circ}(CsSO_4F(c))$ calculated to be -1004.9±1.6 kJ mol^{-1}. The standard potential of the half reaction (9) was estimated to be 2.52±0.05V at 25°C.

$$SO_4F^- + 2H^+ + 2e^- \longrightarrow HSO_4^- + HF \qquad ...(9)$$

Thompson and Appelman[60] have shown that Ag^+ catalysis of oxidation by the fluoroxysulphate ion, SO_4F^-, occurs in aqueous solution and permits the oxidation of Cr^{3+}, Co^{2+} and VO^{2+}. The room temperature fluorination of 1,1-diphenylethene with $CsSO_4F$ results in the formation of the 2-fluoro derivative;[61] norbornene similarly yields 7-fluoronortricyclene and 7-syn-fluoronorborn-2-ene whilst reaction of SO_4F^- with various cyclic enol acetates give α-fluorocycloalkanones in high yield. The same reagent effects fluorine substitution for hydrogen in aromatic compounds : thus phenol gives principally o-fluorophenol.[62] Alkoxybenzenes are similarly fluorinated in the ortho and para positions by $CsSO_4F$ in MeCN in the presence of a catalytic quantity of BF_3,[63] and naphthalene gives 1- and 2-fluoronaphthalenes in the ratio 5:1.[64]

Christe et al.[57] have described the preparation of a hypochlorite derivative of iodine(VII) by reaction (10). The novel cis-

$$CsIF_4O_2 + ClOSO_2F \longrightarrow CsSO_3F + ClOIF_4O \qquad ...(10)$$

and (more stable) trans-bishypohalite compounds (7) and (8) have been prepared by reactions(11) and (12).[65] More reactions of

$$\underset{(trans)}{cis}\ (HO)_2TeF_4 + 2ClF \xrightarrow[(0^{\circ}C)]{-78^{\circ}} \underset{(trans)}{cis}\ \underset{(\underline{7})}{(ClO)_2TeF_4} + 2HF \qquad ...(11)$$

$$(ClO)_2TeF_4 + Br_2 \xrightarrow{-78^{\circ}C} \underset{(\underline{8})}{(BrO)_2TeF_4} + Cl_2 \qquad ...(12)$$

$$CF_3SO_2OX + RX' \longrightarrow CF_3SO_2OR + XX' \qquad ...(13)$$

chlorine(I) and bromine(I) triflates and of $BrOSO_2F$ have been reported by DesMarteau et al.[66] Some of these can be described as electrophilic dehalogenation processes, reaction (13), whereas others are additive in nature. Indeed the chlorine(I) compound effects oxidative addition to CO, SO_2 and SF_4 forming new compounds. Seppelt et al.[67] have shown that $MeOSeF_5$, $CH_2(OSeF_5)_2$, $CH(OSeF_5)_3$, $C(OSeF_5)_4$ and $ClCO(OSeF_5)$ can be prepared from $ClOSeF_5$ and the corresponding halocarbon by a reaction of type (13). Reaction rate coefficients for processes (14)-(16) have been obtained by the modulated photolysis method at 300K and 1 atmosphere total pressure.[68]

$$Cl_2O + Cl \longrightarrow Cl_2 + ClO \qquad \ldots(14)$$

$$ClO + HO_2 \longrightarrow HOCl + O_2 \qquad \ldots(15)$$

$$ClO + HO_2 \longrightarrow HCl + O_3 \qquad \ldots(16)$$

The yield of ClO_2 in irradiated aqueous $NaClO_2$ has been studied as a function of $[ClO_2^-]$.[69] The same radical molecule is formed in the electrolysis of $n\text{-}Bu_4NClO_4$ at high potentials (≥6V) in a number of solvents:[70] this is probably the common intermediate noted recently by a number of workers during the electrolysis of transition metal organometallics.

Schilt[71] has published a comprehensive review of the chemistry of perchlorates, covering the literature up to 1977. The reaction of pure $HClO_4$ with BCl_3 or $BCl_3/MClO_4$ has been used to prepare $BCl_n(ClO_4)_{3-n}$, $n = 0, 1$ or 2, or $MB(ClO_4)_4$, $M = NH_4^+$ or NO_2^+.[72] The i.r. and Raman spectra of the products are all consistent with the presence of strongly bonded unidentate perchlorato groups. The e.s.r. spectrum of $FClO_3^-$ has been observed in SF_6 (isotropic medium) and in anisotropic matrices ($FClO_3$ or Me_4Si).[73] Analysis of the anisotropic spectrum is consistent with a C_{3v} but not a trigonal bipyramidal structure. The unpaired spin density appears to be concentrated in the antibonding $\sigma^*(Cl\text{-}F)$ orbital (3s and $3p_z$ orbitals on Cl and $2p_z$ on F). A lengthened Cl-F bond was implied by the CNDO/2 calculations and indeed dissociation to ClO_3 has been detected in a SF_6 matrix.

$$2BrO \longrightarrow BrOO + Br \qquad \ldots(17)$$

$$2BrO \longrightarrow Br_2 + O_2 \qquad \ldots(18)$$

$$BrO + NO_2 \longrightarrow BrONO_2 \qquad \ldots(19)$$

The rate constants for reactions (17) and (18) have been investigated over the temperature range 223-338K by Sander and Watson.[74] Reaction (19) has been studied by the same group[75] at 298K for the pressure range 1 to 700 torr : they have discussed the implications of their results for the chemistry of the stratosphere.

A bridging bromate ligand has been found in the 8-coordinate Hg(II) compound $K_2Hg(BrO_3)_2(NO_3)_2$:[76] in $Hg(BrO_3)_2.2H_2O$ the mercury atom is bonded to 2 bidentate and 2 monodentate bromate ligands as well as to two water molecules. The crystal structure of $CsBrO_4$ has been determined by single crystal X-ray methods.[77] It adopts a tetragonal structure which is different from that of the lighter alkali metal salts; the Br-O distance in the tetrahedral BrO_4^- ions is 1.591(6)Å.

The reaction of NO with IO to give NO_2 and I has been studied at 298K by the discharge flow/mass spectrometric technique.[58] The analogous reactions of ClO and BrO have been reinvestigated and the results are consistent with the accepted literature values.

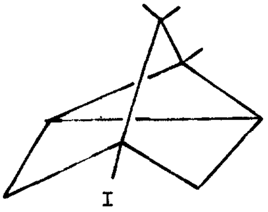
The reactions of CF_3IOF_2 with BF_3, AsF_5 or SbF_5 proceed according to the general equation (20):[78] the reactivity increases along the

$$CF_3IOF_2 + MF_n \longrightarrow CF_4 + IO^+MF_{n+1}^- \qquad ...(20)$$

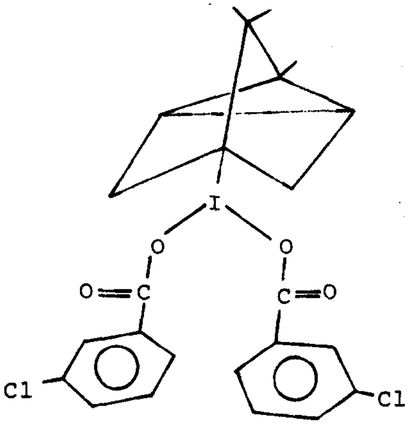
series $SbF_5 < AsF_5 < BF_3$. This kind of behaviour has also been observed with CF_3IF_2 and CF_3IF_4 which both suffer C-I bond cleavage with these fluoride ion acceptors.

The crystal and molecular structures of benzoatopyridineiodine(I) and phthalatobis(pyridineiodine(I)) have been determined by X-ray methods.[79] In the benzoato compound the carboxylato group is unidentate and the molecule is approximately planar. An iodine-(III) dicarboxylate has been prepared (in ca. 65% yield) from 4-iodotricyclene (<u>9</u>) by reaction with three moles of m-chloroperbenzoic acid.[80] The product (<u>10</u>), an unusually stable polyvalent aliphatic iodine compound, melts unchanged at 181°C. Treatment of the I(III) compound with base gave (<u>9</u>) as the principal product, in 50% yield; neither the iodosyl nor the iodyl hydrolysis products could be isolated.

The coordination of iodine in o-iodoxybenzoic acid, $HO_2CC_6H_4IO_2$, is approximately octahedral due to intermolecular contacts with an oxygen of a neighbouring iodoxy group and to



(9)



(10)

inter- and intramolecular bonds to carboxyl oxygens.[81]

Crystalline samples of I_2O_5 and I_2O_4 have been studied by i.r. and Raman spectroscopy in the range 4000-30 cm^{-1}.[82] The spectra of the former compound were assigned and discussed in terms of the recent single crystal X-ray data. However I_2O_4 was shown to have a centrosymmetric unit cell and the spectra were interpreted in terms of iodosyl iodate. The spectra of iodosyl sulphate and selenate were also reconsidered in the light of the established structures. The solubility of $Ca(IO_3)_2$ in molten equimolar $NaNO_3/KNO_3$ in the presence of $Ca(NO_3)_2$ has been measured in the temperature range 523-613K.[83] The shape of the solubility curves can be explained satisfactorily by equilibria between $Ca(IO_3)_2(s)$, $CaIO_3^+$, IO_3^- and Ca^{2+}.

Species containing iodine(VI) are produced by the photolysis or radiolysis of aqueous iodate and periodate solutions.[84] The dominant species formed are IO_4^{2-} and IO_3 for $3 < pH < 7$, $H_5IO_6^-$ and $H_2IO_5^{2-}$ for $8 < pH < 11$, and $H_4IO_6^{2-}$ and HIO_5^{3-} at pH > 12. Symons and Mishra have proposed[85] that the irradiation of octahedrally coordinated periodates at 77K produces both electron-loss and -capture centres : the irradiation of IO_4^- gave similar electron loss centres but markedly different gain centres, probably IO_4^{2-}.

Christe and coworkers[57] have reinvestigated the preparation of cis- and trans-$IF_4O_2^-$ and have shown that a mixture of both isomers is produced in the reactions of $CsIO_4$ with either HF, BrF_5,

ClF_3, ClF_5 or F_2.

7.1.5 Hydrogen Halides

McTigue[86] has pointed out that the extent of the lowering of the vapour pressure of anhydrous HF by an involatile solute is "abnormally" large as a direct consequence of the high degree of association in HF vapour. The electronic solution spectra of U(III), Np(III) and Np(IV) in liquid HF (in the presence of BF_3, AsF_5 or SbF_5) are very similar to those in acidified aqueous solution;[87] however the spectrum of U(IV) is consistent with the presence of UF_2^{2+}. Uranium(V) and neptunium(V) fluoride solutions produced spectra similar to those of the other halo complexes. The solubility of SiF_4, a weaker F^- ion acceptor than HF, in liquid HF and the reversible nature of reaction (21) have

$$Cs_2SiF_6 + 2HF \rightleftharpoons 2CsHF_2 + SiF_4 \qquad \ldots(21)$$

been investigated:[88] it was found possible to synthesise $(NF_4)_2SiF_6$ from SiF_4 and HF solutions of $NF_4^+HF_2^-$. Solvolysis of orthotelluric acid by HF has been reexamined[89] and new information from ^{125}Te n.m.r. spectroscopy has lead to revised interpretation. In particular it is proposed that this reaction yields the thermodynamically favoured isomers whereas the hydrolysis of TeF_6 appears to be governed entirely by kinetics. It is known that hydrogen fluoride catalyses the (explosive) polymerisation of FCN; if FCN is passed into HF at -78°C then the reaction products consist of CF_3CN along with some polymeric material.[90]

The H_2O-HF system has been reinvestigated by Mootz et al.[91,92] and the solidus lines carefully investigated, Figure 2. Two $H_2O.2HF$ phases were detected as well as a metastable phase: the transition between the high and low temperature phases was given as -103°C. The crystal structures of the high temperature 1:2 phase, Figure 3, and of the 1:1 phase,Figure 4, were determined by single crystal X-ray methods. They were found to be oxonium salts, namely $H_3O^+HF_2^-$ and $H_3O^+F^-$ respectively. Mootz also announced his preliminary structural data for the 1:4 compound containing the $H_3F_4^-$ ion.[91] Sommer et al.[93] have used protonated p-methoxybenzaldehyde as an indicator as well as two complementary n.m.r. methods to estimate the base/conjugate acid

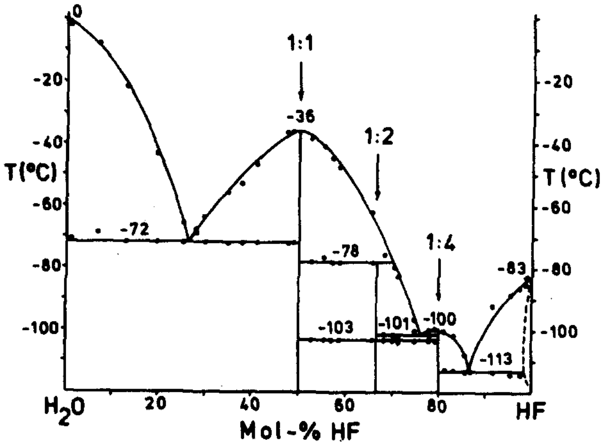


Figure 2. Melting temperature-composition diagram for H_2O-HF (reproduced by permission from Z. Anorg. Allg. Chem., 479(1981)75).

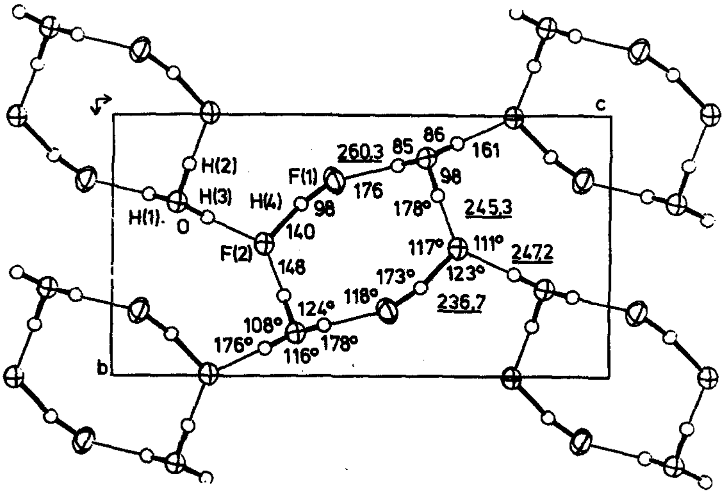


Figure 3. Crystal structure of the $H_2O.2HF$ (high temperature) phase. Bond lengths are in pm, with standard deviations 0.2pm F---F and F---O (underlined) and 5pm for distances to hydrogen (reproduced by permission from Z. Anorg. Allg. Chem., 479(1981)75).

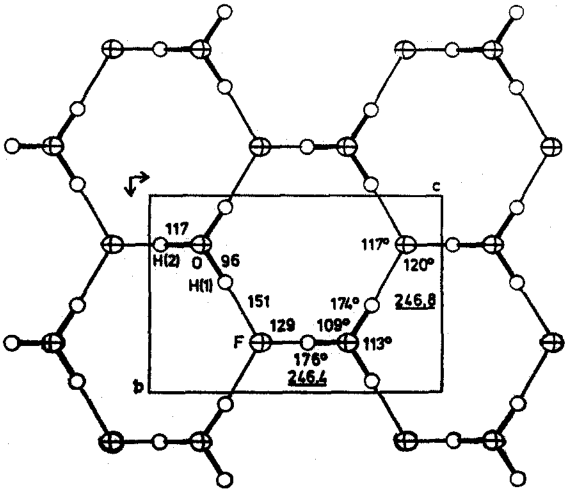


Figure 4. Crystal structure of the $H_2O.HF$ phase. Bond lengths are in pm with standard deviation 0.2pm for O---F (underlined) and 4pm for distances to hydrogen (reproduced by permission from Z. Anorg. Allg. Chem., 479(1981)75).

concentration ratios for the superacid systems $HF-SbF_5$ and HSO_3F-SbF_5.[93] The results confirm the greater acidity of the HF system for corresponding concentrations of SbF_5. Temperature changes and dilution with either SO_2ClF or SO_2 had negligible effects.

Measurements of p, V and T for liquid HCl over the temperature range 188 to 245K have been published:[94] from these the equation of state and the thermodynamic properties of the liquid were evaluated. Silvestri et al.[95] have carried out a preliminary study of electrochemical processes in supercritical HCl. The electrical conductivity of a solution of an electrolyte was found to be lower by one or two orders of magnitude as compared with the subcritical state. It was also remarked that the conductivity is approximately proportional to the specific weight of the supercritical phase. Solutions in HCl of several organophosphorus(V) compounds as well as of $POCl_3$ and H_3PO_4 have been studied by ^{31}P n.m.r. spectroscopy.[96] Phosphoryl compounds were partially protonated but Ph_3PS was not.

7.2 HYDROGEN

Work continues on the decomposition process of hydrogen iodide (derived from H_2O) to liberate H_2. Oosawa has reported on the use of a platinum (supported on active carbon) catalyst column and a temperature cycling system.[97] Yvon et al.[98] have reported on their structural studies of the hydrogen storage material Mg_2NiH_4; neutron powder diffraction data collected at 280°C on the high-temperature modification of the deuteride show it to have a structure resembling the K_2PtCl_6-type. The average distances are Ni-D 1.49(3) and Mg-D 2.305(3)Å. It has been shown that process (22) is the rate limiting step in the reduction of UF_6 by H_2 over

$$UF_6 + H_2 \longrightarrow UF_5 + HF + H \qquad \text{...(22)}$$

the temperature range 625-825K.[99]

The hydrogen bridge in the $[(Me_3Al)_2H]^-$ ion, as the Na^+ salt, is remarkable on account of the Al-H distance (1.65Å) which is shorter than that in the doubly bridged dimer $[Me_2AlH]_2$ (1.68Å).[100] Olah and coworkers[101] have reported that the hydrogenation (deuteration) of non-activated multiple bonds can be effected by means of $Mg/CH_3OH(D)$ in the presence of a Pd-active carbon catalyst : cyclopropyl groups, benzyl ethers and alcohols are examples of groups unaffected under the reaction conditions.

The proton affinities of H_2O (165.3±1.8), C_2H_4 (163.0±1.7), and C_2H_6 (142.1±1.2 kcal mol^{-1}) have been obtained at 298K.[102] Cooks et al.[103] have described the use of a mass spectrometer to determine the affinities of A_1 and A_2 for X in the ion $A_1XA_2^{+/-}$. Although the technique may be extended to the measurement of gas-phase acidities, hydride and metal cation affinities the results here are for proton affinities, e.g. for PhEtNH, 218.7, quinoline 225.8±0.3 kcal mol^{-1}.

The acidity function H_o for pentafluorobenzenesulphonic acid in aqueous solution (up to 85%) have been determined by Habel and Sartori.[104] The extrapolation to 100% gives a value of -3.98 for H_o signifying that the acid is more than a factor of ten weaker than H_3PO_4. A dynamic n.m.r. study of the rate of proton exchange between HSO_3F and protonated solute bases has been used to derive pK differences, between bases, and the approximate course of an acidity function between 0 and 90 mol% SbF_5.[105] Gold and coworkers conclude that the acidity increases monotonically over this range.

It has been postulated that molecules with anaesthetic potency are able to perturb or dissociate hydrogen bonds and that this is a factor in the mechanism of anaesthetics. Hence Sandorfy et al.[106] have examined by quantum chemical and statistical thermodynamic means the equilibria for $(H_2O)_2$ interacting with $CHCl_3$ or $c\text{-}C_3H_6$, two potent anaesthetics, or with CHF_3 (no anaesthetic potency). It was claimed that the resulting ΔG^o values for the dimer dissociation process and the extent of mixed dimer formation parallel the known anaesthetic potencies of the three compounds. An analysis of the geometry of one hundred O-H---O hydrogen bonds, all previously studied by neutron diffraction, has shown the following features:[107] (i) 25 are bifurcated, thus showing this mode is commoner than previously supposed, (ii) for the linear bonds examined the O_a---H distance tends to be shorter when the donor (O_d) is also an H-bond acceptor and the acceptor (O_a) is also an H-bond donor, (iii) the O_d-H---O_a angle tends to be closer to 180° for short O_a---H bonds than for long ones. A statistical analysis of the X-ray data on the (weak) intermolecular hydrogen bond in organic homomolecular crystals has been reported.[108] The average lengths observed for different types of bonds correlate well with the sum of the van der Waals radii for the electronegative atoms involved. Pimentel and McClellan had drawn the same conclusion in 1971 although they used a different radius for nitrogen.

The so-called hexahydrates of HMF_6, M = P, As or Sb, have been compared by Davidson et al.[109] and are shown to be probably isostructural: the ^{19}F n.m.r. spectra clearly show the presence of one molecule of HF for each hexafluoride anion. These solids appear to form clathrate-type hydrates in which disordered MF_6^- ions occupy cages in a fully H-bonded host lattice formed by H_2O, H_3O^+ and HF. The proposed composition is $HMF_6.HF.5H_2O$. X-ray diffraction has provided the first evidence for the existence of the homoconjugated anion $[O_2FSO\text{--}H\text{-}OSFO_2]^-$ containing a very short and symmetrical hydrogen bond (O--H--O, 2.41(1)Å).[110] Di-p-methylphenylphosphoric acid, $(p\text{-}MeC_6H_4O)_2PO(OH)$, has been characterised in the solid state by X-ray analysis.[111] Two acid molecules are linked together by strong, short (2.512(3)Å), apparently centred, hydrogen bonds. A powder neutron diffraction study of the good proton conductor $DUO_2AsO_4.4H_2O$ at 305K has shown the presence of $D_5O_2{}^+$ ions and indicates hydrogen ordering effects in the plane of the water molecules.[112] The $H_5O_2{}^+$ ion has also been found in the solid state structure of $[H_5O_2][Ru(CO)_3Cl_3].SbCl_3$;[113] the O-H---O distance is 2.37(1)Å. The hydrated hydroxide ion, $H_3O_2{}^-$, has been characterised structurally in the crystalline state. A novel situation for this species has been reported by Bino and Gibson[114] who have obtained three complexes $\{[M_3O_2(O_2CEt)_6(H_2O)_2]_2(H_3O_2)\}Br_3.6H_2O$, M = Mo or W, in which H_3O_2 functions as a bridging ligand.

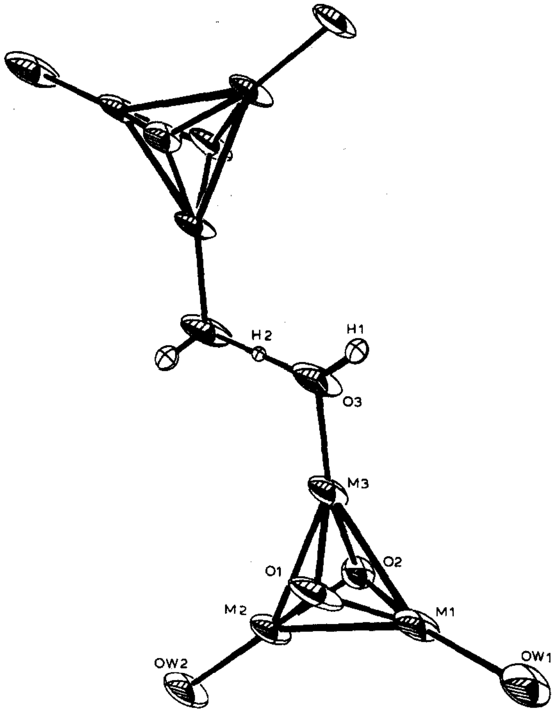


Figure 5.

The skeletal structure of $\{[M_3O_2(O_2CEt)_6(H_2O)_2]_2(H_3O_2)\}^{3+}$ The propionato groups have been omitted (reproduced by permission from J. Am. Chem. Soc., 103(1981)6742).

Brown et al.[115] have presented ^{17}O n.q.r. data for several H-bonded systems. The experimental data support the results of a previous theoretical study and show that the technique is valuable for the study of O-H---O interactions in the solid state. A neutron diffraction study of lithium hydrogen phthalate methanolate has revealed two very short H-bonds;[116] one is virtually centred, O-H---O 2.393(4)Å, and the other is significantly dissymmetric, 2.388(4)Å. The distortion in the second type probably arises from minor differences in the coordination geometries around the two carboxyl groups. The compounds $(dma)_2HMF_6$, M = P, As or Sb, dma = dimethylacetamide, have been investigated by i.r., ^1H and ^{19}F n.m.r. spectroscopy.[117] The spectroscopic data are consistent with the presence of short H-bonds, O-H---O 2.419(4) and 2.443(7)Å, in the P and Sb compounds.

Ab initio LCAO-MO-SCF calculations have been carried out on the ions $H_nF_{n+1}^-$, n = 1-4, and the polymeric species $(HF)_m$, m = 1-4, to determine molecular configurations and H-bond energies.[118] The anions have structures in which a central fluoride acts as the proton acceptor to between one and four HF molecules. The HF polymers, on the other hand, prefer open chain arrangements. The same authors also report a "safe", simple synthesis of KHF_2 starting from KF; using a solution containing equal weights of H_2O and acetic acid, equation (23), a yield of up to 98% KHF_2 was

$$2KF + H_2O + CH_3CO_2H \rightarrow KHF_2\downarrow + CH_3CO_2K + H_2O \qquad ...(23)$$

obtained. Deuteration of $KF.(CH_2CO_2H)_2$ causes no significant change in the bond lengths only a decrease in the bond angle at the fluorine.[28] Reference has already been made above (section 7.1.2) to other calculations of H-bonded systems involving F^- and to the possibility of biological effects of the binding of peptides.[29]

Oxonium tetrafluoroborate, $H_3O^+BF_4^-$, has been shown by Mootz and Steffen[119] to have an H-bonded structure with O-H---F distnaces ranging from 2.58 to 2.61Å. Only three of the fluorines of BF_4^- participate in this bonding which generates rings fused together to form a one dimensional chain structure. The dihydrate contains $H_5O_2^+$ and BF_4^- in which the H-bonded network is three dimensional : the O-H---O distance in $H_5O_2^+$ is 2.41Å. A related but novel oxonium cation is present in $HBF_4.2MeOH$.[119,120] The crystal structure contains dimeric H-bonded cations $Me_2O_2H_3^+$ linked together, via BF_4^-, through O-H---F bonds, as shown in Figure 6.

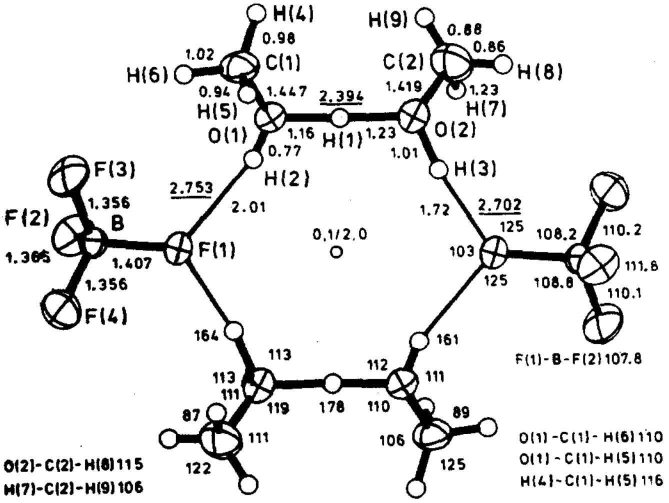
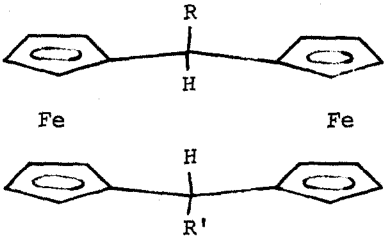


Figure 6. The centrosymmetric cyclic dimer unit of the $HBF_4.2MeOH$ structure. Standard deviations (for atoms other than protons) 0.003-0.004Å and 0.3° : O---F distances underlined (reproduced by permission from Z. Anorg. Allg. Chem., 482(1981)193).

The crystal structures of the two newly studied[92] oxonium salts $H_3O^+HF_2^-$ and $H_3O^+F^-$ have been mentioned in Section 7.1.5. Both form H-bonded structures, Figures 3 and 4; the former phase adopts a layer structure with six-membered rings of composition $2(H_3O^+HF_2^-)$ whereas the 1:1 compound has a puckered layer structure with $3(H_3O^+F^-)$ rings having chair conformations. The crystal structures of $BF_3.H_2O$ (at -35°C) and of the methanol analogue, methoxytrifluoroboric acid (at -40°C) have been determined by Mootz and Steffen.[121] The same workers have reinvestigated[122] the structure of $BF_3.2H_2O$; the compound should clearly be formulated as the monohydrate of hydroxytrifluoroboric acid, $(BF_3OH_2)H_2O$ rather than $H_3O[BF_3OH]$.

The ^{14}N quadrupole and H-F spin-spin coupling in MeCN-HF have been measured from the microwave rotational spectra.[123] Bonner[124] has reported evidence from osmotic and activity coefficients as well as from (^{19}F and ^{13}C) n.m.r. spectroscopy consistent with an H-bonded interaction between the CF_3 group of the triflate ion and H_3O^+ and tetramethylguanidinium ions. The methanesulphonate analogues were used as comparators. Mueller-Westerhoff et al.[125] have described n.m.r. evidence for the formation of C-H---C hydrogen bonding in the monocarbanions (12a,b,c) of the [1.1] ferrocenophanes (11a,b,c).



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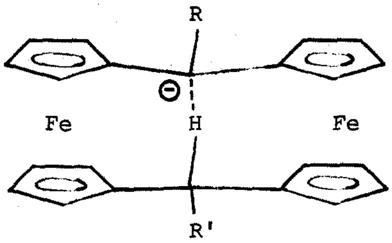

(12)

a R = H; R' = H
b R = H; R' = Me
c R = Me; R' = Me

The crystal structure of diphenyldithiophosphinic acid $Ph_2PS(SH)$ has been determined at 140 and 293K.[126] Molecules of the acid are linked together by nearly linear (ca. 170°) S-H---S bonds to form endless helical chains. At 140K the S-H---S distance is 3.790(1)Å. The crystal structure of $(Et_3NH)_2SnCl_6$ has been determined and shows stronger H-bonding than the corresponding ammonium salt.[127] The Et_3NH^+ cation shows nearly symmetrical bifurcated bonding to two chlorines of the neighbouring $SnCl_6^{2-}$ ions (NHCl angles 138 and 136(3)°). Trans-$SnCl_4.2C_6H_{11}OH$ crystallises with two additional alcohol molecules of which the oxygens function as basic groups and H-bond to the ligand alcohol molecules (O-H---O, 2.57Å);[128] there is also a weak interaction (3.39Å) between O and Cl of a neighbouring molecule.

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