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Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 HALOGENS

7.1.1 The Elements

The proceedings of a symposium, organised by the Inorganic Chemicals Group of the Industrial Division of the Chemical Society which took place in London in 1977, have been published.[1] The book contains useful articles on (i) the Chlor-Alkali industry, (ii) Chlorine and Chlorination, (iii) Hydrofluoric acid, Inorganic Fluorides and Fluorine, and (iv) Bromine and the Bromine-Chemicals Industry. A new edition of Ullmann's Encyclopedia of Technical Chemistry appeared in 1976 : the article by Wechsberg *et al.*[2] reviews in depth the industrially significant properties of fluorine and inorganic fluorine compounds. ^{19}F coupling constants have been reviewed by Emsley *et al.* :[3] this complements the earlier review on ^{19}F chemical shifts. The new review tabulates most of the data published up to 1972.

The manufacture of F_2 has been reviewed by Royston and Ring:[4] the purification of commercial grade F_2 gas can be achieved by (a) conversion of O_2 to non-volatile O_2^+ salts and (b) a 70K to 63K trap-to-trap distillation.[5] Pyrolysis of CoF_3 generates CoF_2 and releases F_2 in yields not exceeding 6.7% of theory on account of losses due to reactions with the surface of the reaction vessel.[6]

The low-temperature fluorination of Me_4Sn in a cryogenic-zone reactor can be used to prepare $Me_3Sn(CH_2F)$, $Me_3Sn(CHF_2)$, $Me_2Sn(CH_2F)_2$ as well as trifluoromethyltin(IV) compounds.[7] The reaction between NH_3 and F_2 takes place at or above -120^oC.[8] The products were shown to be NH_4F, NHF_2, NF_3, N_2F_4, N_2F_2 and N_2. The reaction takes place only in the gas phase and the possibility that fluoramine, NH_2F, is formed as a reactive intermediate cannot be excluded. The kinetics of the fluorination of sintered PuO_2 pellets to PuF_6 by F_2 have been investigated in the temperature range 350-550^oC.[9]

Lentz and Seppelt[10] have produced some interesting evidence to show that the $OSeF_5$ and $OTeF_5$ ligands have higher electronegativity values than fluorine itself. They have found that in the series of compounds $IF_x(OSeF_5)_{5-x}$ and $IF_x(OTeF_5)_{5-x}$, $1 \leq x < 5$, that F preferentially occupies the axial position and thus, according to the rules of the electron pair repulsion theory, must be the less electronegative ligand.

The gas phase Lewis acidities towards F^- of the following have been inferred from an ion cyclotron resonance study : CO_2, 33; COF_2, 35; CH_3COF, 38; CH_2=$CHF \cdot CH_3$, 15 (all ±3) kcal mol^{-1}.[11] An ^{18}F recovery system using an anion-exchanger has been described for the $H_2^{18}O$ target at the ORNL 86in. cyclotron.[12] When irradiated with 27.5 MeV ^3He particles a Ne-H_2(2%) gas mixture yields carrier-free $H^{18}F$, which could be collected in a -15^oC trap.[13] The methodology and targetry of for the production of ^{18}F labelled F_2, CF_4, HF, NOF, and ClF have been described by Lambrecht _et al._[14] The same workers[15] have also developed a convenient procedure for the rapid synthesis of 18F-labelled ^{18}F-labelled CF_3OF : CsF was found to be a good catalyst for the synthesis of ^{18}F-CF_3OF-^{18}F. The ^{18}F exchange characteristics of MF(M=Cs, Ag, Tl, ½Hg_2), HgF_2, LaF_3 and TlF_3 with $S^{18}F_4$ and $^{18}F_2CO$ have been determined.[16] Although the behaviour of TlF, Hg_2F_2, HgF_2 and LaF_3 suggests that they might be good catalysts in the formation of SF_5Cl from SF_4, these ionic fluorides show no catalytic activity.

The intercalation process of Br_2 in graphite has been discussed by Young[17] who points out that as rapid intercalation progresses the charge transferred per Br_2 is significantly reduced. Isolable crown ether complexes of Br_2 have been shown to effect highly stereoselective brominations of _cis_- and _trans_-β-methylstyrene.[18] Highly conducting solids ($\sigma \sim 30\Omega^{-1}cm^{-1}$) are formed by the room temperature reaction of the insulator S_4N_4 ($\sigma=10^{-4}\Omega^{-1}$ at 25°C) with gaseous Br_2, ICl, or IBr, and with I_2 at 125°C.[19] On the other hand the orange-yellow insulator $S_4N_3^+Br_3^-$ is produced when S_4N_4 reacts with liquid Br_2;[20] with liquid ICl the analogous ICl_2^- salt is formed.

7.1.2 Halides

A study of the CsF-RbF-EtOH system at 25°C has shown that the separation of CsF from RbF by crystallisation from solutions in EtOH is possible:[21] the solvate CsF.EtOH is formed whereas RbF does not form a stable ethanolate at this temperature. Melts of TeO_2 with NaF or KF yield the monofluorotellurite compounds $MTeO_2F$, M=Na or K, rather than $M_2TeO_2F_2$ which are formed by RbF or CsF.[22] The dynamic response of the fluoride ion-selective electrode has been discussed by Hawkings et. al.;[23] of the four distinct processes involved the calibration drift process was claimed to be the major obstacle limiting the amount of F^- detectable. A model was presented which explains many of the anomalies of electrode behaviour reported in the literature. The stability trend

$$MgF^+ > CaF^+ > SrF^+ > BaF^+$$

already established for the alkaline earth monofluorides in aqueous solution has also been observed in methanol.[24] Moreover the stabilities are enhanced by comparison with the aqueous system especially for the smaller alkaline earths. The coefficient of self-diffusion of F^- in molten $LiBeF_3$ [25a] is comparable with that in Li_2BeF_4 [25b] and significantly greater than that in Flinak (LiF-NaF-KF eutectic) at temperatures above 570°C. Moreover the activation energy for self-diffusion is also greater for $LiBeF_3$ (29.4 kcal mol^{-1}) than for Flinak (5.0 kcal mol^{-1}). No explanation was offered for these results.

Clark and Miller[26] have reported rapid and efficient mono-C-alkylation of a number of enolisable β-dicarbonyl compounds by alkyl iodides using the strongly H-bonded monosolvates formed between the enolised β-dicarbonyl and the powerful H-bond electron donor tetraethylammonium fluoride. They found no apparent contamination due to the formation of O-alkyl, dialkyl or polymerisation products. Owing to their extremely hygroscopic nature these tetraalkylammonium fluorides are not easily dehydrated. A very simple process which renders them apparently anhydrous has been described by Clark.[27] The fluoride is adsorbed exothermally from aqueous solution on to silica gel and the water removed under reduced pressure : the product is stable, non-hygroscopic and functions as a convenient source of anhydrous fluoride ion for a range of organic reactions.

The $^{19}F(p,\alpha\gamma)^{16}O$ nuclear resonant reaction has been successfully applied to the measurement of the spatial distribution and depth profile of the fluorine concentration on the surface of fluorinated polyethylene.[28] The technique is readily applicable to layers of other elements on other materials, including teeth.

Kolditz et al.[29] have surveyed heterogeneous catalyst systems for Cl-F exchange reactions involving HF, with particular regard to halogenated ethanes. In a note elsewhere the group discuss the use of hexafluorosilicates for such exchange reactions.[30] An early review by Thrush[31] of the chemistry of the stratosphere calls for a fuller knowledge of atmospheric processes and of the biological effects of prolonged exposure to intensified u.v. radiation. A recent and interesting contribution to this discussion is a note describing evidence for the photolytic decomposition of chlorofluorocarbons adsorbed on silica gel : although an extrapolation of the results to the troposphere cannot be justified they do confirm that the decomposition is comparable with that of several methyl- and chloro-benzenes (poorly degradable) rather than with chloro-ethanes and -propenes (easily degradable).[32]

Complex formation between SO_2 and X^- (X=Cl, Br, or I) in solution in MeCN or DMSO has been studied by vapour pressure measurements and calorimetry.[33] These results show that there is clear trend in thermodynamic values ($-\Delta H^o$, kcal mol^{-1}) for the series SO_2Cl^-, SO_2Br^- and SO_2I^- (4.11, 3.42, 3.05, respectively) which was not apparent in earlier reports.

7.1.3 Interhalogens and Related Species

Schack and Christe[34] have reviewed the chemistry of electropositive chlorine compounds, such as ClF, SF_5OCl, and $ClONO_2$, with fluorocarbons. Most reactions involve addition of Cl-X across multiple bonds or oxidative addition to atoms such as I or S in their lower oxidation states. Shamir[35] has reviewed fluorohalogen anions, their preparations, properties and structures. The low temperature reactions of ClF with CF_3SO_3H and CF_3CO_2H have been shown to yield the previously unknown chlorine(I) derivatives.[36] Yields of the pale yellow products are quantitative, equation (1), X=SO or C, on a 10 mmolar scale. Both compounds are

$$CF_3XO_2H \; + \; ClF \xrightarrow{-111 \text{ to } -78^{o}C} CF_3XO_2Cl \; + \; HF \qquad (1)$$

somewhat unstable at 22°C and yield CF_3Cl and SO_3 or CO_2; CF_3CO_2Cl will explode at pressures above ca. 50 torr. Chlorine trifluoromethanesulphonate is claimed to be the most electrophilic chlorine compound ever prepared. Tetra-n-butylammonium chloride has a retarding effect at high concentrations on aromatic chlorination in chloroform.[37] This has been attributed to the formation of Cl_3^- for which the formation constant was shown spectrophotometrically to be 17 ± 3 M^{-1}.

In a photochemical study of the H_2-ClF reaction at 20°C the investigators concluded that the rate for reaction (2) is ca. 6 times faster than that for reaction (3).[38] In the u.v. induced

$$H \; + \; ClF \longrightarrow HCl \; + \; F \qquad (2)$$

$$H \; + \; ClF \longrightarrow HF \; + \; Cl \qquad (3)$$

$$F \; + \; ClF \longrightarrow ClF_2 \qquad (4)$$

reaction of HCl with ClF the chain termination apparently depends on process (4), for which the rate constant is 4.5×10^{-4} cm^3 s^{-1} at 20°C.[39]

Raman, i.r. and u.v. spectra of the ClF_2 free radical have been obtained in solid N_2.[40] In the molecular spectra mutual exclusion was observed and, indeed, the data do not exclude a linear geometry; nevertheless a slightly bent geometry was suggested and a lower limit of 136° for the FClF angle was calculated from isotopic ν_3 splittings. Infrared and laser-Raman studies have been performed on the X_2-F_2 system, X=Cl, Br or I, in Ar matrixes.[41] Mercury arc photolysis produced the new species XF_2, X_2F and X_2F_2 as well as BrF or IF_3. The symmetrical, T-shaped XXF_2 species is the dominant product in all three studies.

The interaction of graphite with solutions of ClF_3 in NOF.3HF yields the intercalation compound of approximate composition $C_{14}F.ClF_3.3HF$.[42] Undiluted chlorine trifluoride fluorinates graphite, liberating ClF, and forms typically an intercalate such as $C_{31}ClF_8$:[43] chlorine(V) fluoride intercalates to yield typically $C_{7.6}ClF_{4.3}$, which decomposes thermally liberating Cl_2, fluorocarbons and even ClF and ClF_3.

The structure of ClF_5 in the gas phase has been investigated by electron diffraction;[44] the results are in good agreement with the bond length and angle parameters calculated from the microwave studies in 1976.[45] The existence of three solid phases of ClF_5 has been confirmed and Raman spectra measured and interpreted for each.[46] Sukhoverkhov and Barkman[47] have studied mixtures of ClF_5 and HF by d.t.a. The binary system unexpectedly shows complete insolubility of its components in the solid and liquid states. The low temperature part of the phase diagram consisted of three lines at $-105^{o}C$, $-90^{o}C$ and $-83^{o}C$ corresponding to $\beta \rightarrow \alpha$ ClF_5 transition, the melting of ClF_5, and the melting of HF, respectively (the $\gamma \rightarrow \beta$ ClF_5 transition was not observed). The higher temperature part of the phase diagram shows that the two liquids are immiscible at temperatures below $+4(\pm 4)^{o}C$.

The products and kinetics of addition of bromonium[48] and iodonium[49] nitrates to a variety of unsaturated organic substrates have been investigated by Lown and Joshua. Evidence for the association of $BrOSO_2F$ in $S_2O_5F_2$ has been obtained from Raman and i.r. studies.[50] The He(I) photoelectron spectra of BrF and IF have been recorded and interpreted;[51] estimates of r_e, $\bar{\omega}_e$ and D_e have been made for the +1 ions.

Intercalation of BrF_3 and BrF_5 into graphite is accompanied by extensive fluorination with the formation of $C_{24}BrF_{13}$ or similar compositions in both instances.[43] Thermal decomposition gave only Br_2 and fluorocarbons, i.e. no bromine fluorides. A study of the PtF_4-BrF_3 system by d.t.a. has been carried out in nickel tubes.[52] Two incongruently melting compounds, 1:2 and 1:7, were detected at PtF_4 concentrations up to 43 mol %. Fluorine n.m.r. spectra of the 1:1 complexes of BrF_3 with BF_3 and PF_5, under conditions of slow fluorine exchange, show two F-on-Br resonances in SO_2ClF.[53] Cyr and Brownstein interpret this as arising from structure (1), for the BF_3 adduct, rather than from a structure in which an F on bromine is

$$F - \underset{\overset{|}{F}}{Br^{+}} \cdots\cdots F - BF_3$$

(1)

associated with the solvent. Solubility data has been reported for the BrF_3-RbF-HF system at $20^{o}C$.[54] The solubility of RbF in BF_3 is 9.2wt% but is greatly enhanced by the addition of HF. Apart from RbF.3.5HF, two fluorobromate phases were reported, $RbF.2BrF_3$ and $RbF.BrF_3$. The BrF_5-SbF_5 system has been examined by d.t.a..[55] The formation of five double compounds was inferred; however, all but the

1:2 compound melt incongruently. The melting point, 81°C, observed for this adduct is higher than that previously reported.

The crossed beam reactions of F_2 with I_2, ICl or HI have produced three triatomic radicals.[56] The first of these, IIF, is 3kcal mol^{-1} more stable than I + IF, being stabilised primarily by the II-F bond. Of the other two radicals, ClIF and HIF, the latter is mainly stabilised by the H-IF bond. The solvent effect on equilibrium (5)

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (5)$$

has been investigated by means of calorimetry and potentiometry in aprotic solvents.[57] In addition values of the enthalpy of formation of two solid triiodides were obtained which, together with values for other triiodides, cast doubt on calculated lattice enthalpies and the formation enthalpy of I_3^- in the gas phase. The latter is now found to be more negative than -22kcal mol^{-1}. The novel salt (2) is precipitated as a fine yellow solid from solution;[58] although (2) is

$$2Me_2NCl + 2MeI \xrightarrow{MeI} [Me_4N]^+[Me_4N(ICl)_2]^-$$

(2)

unstable at 20°C, the crystal structure has been determined by X-ray methods at -60°C and the anion was shown to have the structure shown in Figure 1.

The i.r. and Raman spectra of IN_3 in solid CH_2Cl_2 are consistent with a C_s molecular symmetry for this light-sensitive molecule.[59] The standard enthalpies of formation of crystalline $MICl_2$, M=Cs or Rb, have been determined as -511 and -491 (both ±4) kJ mol^{-1} respectively, based on the reaction enthalpies of processes (6) and (7).[60] ^{35}Cl n.q.r. spectroscopy has been shown to be sensitive to

$$5ICl_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Cl^- + 6H^+ \qquad (6)$$

$$3I_2 + 6Ag^+ + 3H_2O \longrightarrow 5AgI + 6H^+ + AgIO_3 \qquad (7)$$

distortions of ICl_4^- whether caused by cation-anion interactions or by phase transitions :[61] the average frequency for ICl_4^- derivatives was found to be 22.6 MHz. The orange crystalline compound Cl_7IS has been shown recently to be $[SCl_3]^+[ICl_4]$.[62] Crystallographic methods have now confirmed this and show that the anion is slightly distorted

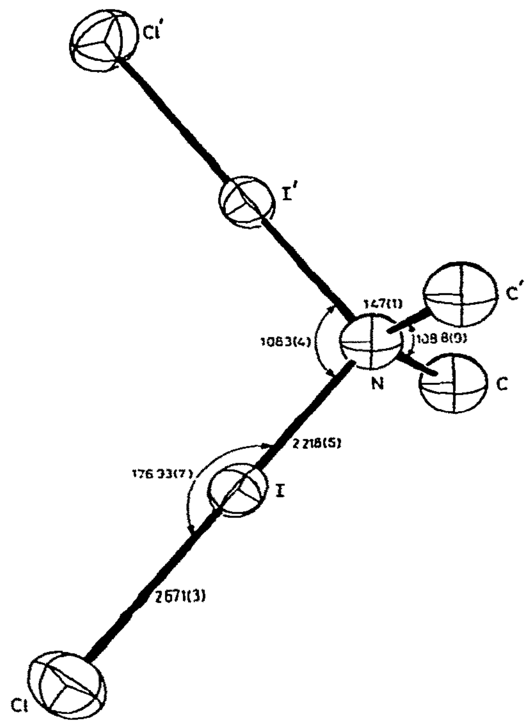
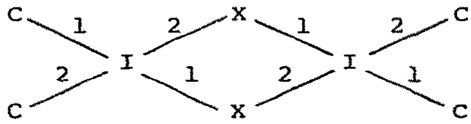


Figure 1. The structure of the $[Me_2N(ICl)_2]^-$ ion. Primed atoms are related to unprimed ones by the crystallographic 2-fold axis. Bond distances are in Å. (Reproduced by permission from J. Chem. Soc. Chem. Commun., (1977)403.)

from D_{4h} symmetry due to cation-anion interactions.[63] The crystal and molecular structures of $[Ph_2IX]_2$, X=Cl, Br or I, have been determined by X-ray methods;[64] the three compounds are isomorphous and show the overall structure of centro-symmetric dimers held together by halogen bridges, which are nearly symmetrical. The I-X distances exceed those of the corresponding gaseous IX molecules by about 0.77Å, see Table 1, so that the bonding is described in terms of secondary bonds (I----X) holding $[Ph_2I]^+$ and X^- units together.

Table 1. Bond lengths (Å) and angles(°) with standard deviations in parentheses. Bonds 1 and 2 are arranged as follows, with $(C-I)_1$ shorter than $(C-I)_2$.



X		C-I	I-X	$(I-X)_{single}$	Ref.	$(I-X)_{obs.}$ - $(I-X)_{single}$
Cl	1	2.078(6)	3.064(3)			
	2	2.096(7)	3.105(3)			
	Mean	2.087	3.085	2.321	a	0.764
Br	1	2.071(10)	3.253(2)			
	2	2.095(13)	3.248(3)			
	Mean	2.083	3.250	2.485	b	0.765
I	1	2.095(9)	3.453(2)			
	2	2.103(9)	3.421(2)			
	Mean	2.099	3.437	2.667	c	0.770
		C-I-C	X-I-X	I-X-I		X-I-C
Cl		92.6(3)	93.48(7)	86.52(7)		179.3(3) 177.3(2)
Br		91.8(6)	92.54(6)	87.46(6)		177.0(4) 176.5(5)
I		93.2(5)	91.91(3)	88.10(3)		177.8(3) 174.8(4)

(a) E.Hulthen, N.Johansson, and U.Pilsäter, Arkiv. Fys., 14(1959)31; (b) T.S.Jaseja, J. Mol. Spectrosc., 5(1960)445; (c) D.H.Rank and W.M. Baldwin, J. Chem. Phys., 19(1951)1210.

Diphenyldiodonium salts, Ph_2IY, Y=Cl or BF_4, react readily with $[IrX(CO)(PR_3)_2]$ (X=Cl, Br; PR_3=PPh_3 or $PMePh_2$) to yield iridium(III) σ-phenyl complex of general composition $[IrXYPh(CO)(PR_3)_2]$.[65] The vibrational spectra of $I(CF_3CO_2)_3$ as the solid, in solution and in the gaseous state have been reported.[66] The Raman spectrum of the vapour is consistent with symmetrical bidentate coordination of trifluoroacetato groups; however in the solid and in solution in MeCN the ligand is monodentate.

In a study of IF_5 at 140 and 210 GHz 318 transitions were observed and 5 molecular parameters were calculated with high accuracy.[67]

The enthalpies of sublimation and of melting of IF_5 have been revised by Meixner et al. to 48.1 and 5.0 kJ mol^{-1}, respectively.[68] N.q.r. spectra, ^{127}I, ^{121}Sb and ^{123}Sb, of IF_5, $IF_5.SbF_5$, $IF_5.2SbF_5$, $CsIF_6$, $RbIF_6$ at 77K have been reported.[69] The results for IF_5 are in reasonable agreement with the available structural data. ^{127}I n.q.r. data for IF_6^- were said to be consistent with an axially symmetrical field gradient.

The tendency of IF_5 to form adducts with donors such as MeCN, 1,4-dioxan, and F^- has been discussed:[70] the authors point out that the distinction between $M^+IF_6^-$ and molecular $MF.IF_5$ species may not always be clearcut. A reaction involving the oxidation of Tl(I) to Tl(III) by IF_5 in MeCN but not in liquid IF_5 implies that IF_5 is a more effective oxidiser in MeCN than is WF_6. The reaction of IF_5 and $B(OTeF_5)_3$ proceeds in the limit according to equation (8);[10] the

$$3IF_5 + 4B(OTeF_5)_3 \xrightarrow{20^\circ C} \underset{(\underline{3})}{3FI(OTeF_5)_4} + 4BF_3 \quad (8)$$

$$FI(OTeF_5)_4 \xrightarrow{80^\circ C} O{=}I(OTeF_5)_3 + TeF_6 \quad (9)$$

$$I(OTeF_5)_3 + Xe(OTeF_5)_2 \xrightarrow{20^\circ C, h\nu} \underset{(\underline{4})}{I(OTeF_5)_5} + Xe \quad (10)$$

significance of the substitution-inert axial F on compound (3) has been discussed at the beginning of this Chapter. Compound (3) decomposes at 80°C under more forcing conditions, equation (9). The fully substituted iodine(V) compound (4) was also prepared according to reaction (10). Compound (4) dissolved in IF_5 formed numerous exchange products of the series $F_xI(OTeF_5)_{5-x}$ whose selenium analogues could be prepared by ligand transfer with $F_2OPOSeF_5$.

Iodine(V) fluoride is intercalated by graphite only in the presence of HF:[43] a typical product had the composition C_8IF_5, from which could IF_5 be desorbed on heating. ^{19}F n.m.r. spectroscopy of the graphite intercalation product of IF_7 implies that iodine reduction accompanies intercalation;[71] a later publication has confirmed that graphite fluorination occurs in this process and indeed IF_5 and fluorocarbons are formed on desorption.[43]

Calorimetric and n.m.r. spectroscopic studies of IF_7 over the temperature range 77-300K have shown four phase transitions at 84, 148, 195-220 (second order), and 271K.[72] The vapour pressure of IF_7 has been measured over the range 192-305K in a static system.[68] The results for liquid IF_7 (equation (11)) are 20-30 torr higher than

$$p(\text{torr}) = \exp(62.60379 - 7391.581/T - 0.1540393T + 0.000173463T^2) \quad (11)$$

those previously published. Unstable 1:1 adducts are formed by IF_7 with NOF and NO_2F;[73] the compounds are completely dissociated in the vapour phase.

7.1.4 Oxides, Oxide Halides, and Oxyanions

New calculations for O_2F_2 have produced more satisfactory molecular parameters:[74] nevertheless the O-O and O-F bond distances are respectively 0.07Å longer and 0.08Å shorter than the experimental values. Such discrepancies are without precedent for this level of calculation. Using *ab initio* Gaussian SCF and CI methods the geometry, binding energy and dipole moment have been calculated for both ONF and NOF.[75] The preparation of $(CF_3)_3COOF$ has been achieved by the low temperature reaction of F_2 with the novel anion, $(CF_3)_3COO^-$, which was generated *in situ* by nucleophilic attack of F^- on $(CF_3)_3COOSO_2F$.[76] The new compound decomposes very slowly at 22°C and 30mm pressure, although the liquid phase may explode at this temperature.

The reaction between ClO_2 and sulphur(IV) has been investigated in the pH range 8-13 under conditions which avoid the rapid successive reduction by sulphur(IV) in acidic solution of the chlorous and hypochlorous acid intermediates.[77] In alkaline solution the major products were found to be chlorite and sulphate.

X-ray and neutron diffraction studies of powdered ClO_2F are compatible with a monoclinic cell, space group P2/m, related to the orthorhombic cell of Cl_3.[78] The reaction between hydroxylamine and ClO_3F in EtOH proceeds largely according to equation (12).[79]

$$6NH_2OH + 2ClO_3F \longrightarrow 2(NH_3OH)F + 2(NH_3OH)ClO_3 + H_2O + N_2 + \tfrac{1}{2}O_2 \quad (12)$$

Rozen *et al.* have studied the extraction of perchloric acid in the concentration range 0.1 - 8.6M by 0.025M solutions of $S,R_2P(O)CH_2P(O)R'_2$, (R=Ph or C_8H_{17}, R'=Ph or C_8H_{17}), in CCl_4 or dichloroethane.[80] The results were found to be consistent with the extraction of $HClO_4.nS$ (n = 2, 1 and 0.5). Evidence has been obtained for the existence of a 1:1 adduct between HF and $HClO_4$ which melts incongruently at $-117^{o}C$.[81] I.r. spectroscopy of this system was said to indicate that $HClO_4$ is weakly H-bonded to HF polymers in much a way that HF is acting as the base. The perchloratocobaltates, $M[Co(ClO_4)_3]$, M = Cs, Rb or NH_4, decompose in contact with liquid anhydrous $HClO_4$ to form soluble $MClO_4$ and insoluble $Co(ClO_4)_2$;[82] the latter decomposes thermally at 210-250°C to Co_3O_4, Cl_2 and O_2. Preliminary results from a study of the longtitudinal and transverse relaxation times of the ^{35}Cl nucleus in ClO_4^- at 28°C in aqueous solution show that this is a very sensitive method for investigating the interactions with cations.[83]

The simultaneous condensation of Br atoms, O_2 molecules and excess Ar on to a surface at 10K generates the previously unknown O_2Br radical.[84] There are three bands in the 1400-1500 cm^{-1} region corresponding to $\nu(\dot{O}-O)$ of this radical for 45% ^{18}O-enriched material. Since the centre band is only slightly broadened, see Figure 2, the expected non-equivalence of the two oxygens could not be confirmed.

Jacob[85] has shown that BrF_5 and H_2O in the molar ratio 5:1 react over the temperature range -196^{o} to $-60^{o}C$ to form BrO_2F almost quantitatively. This represents an improved synthesis and is especially suitable for the preparation of ^{18}O-labelled material. I.r. spectra in an Ar matrix, in the solid state and, in addition, good quality spectra from gaseous material were obtained in spite of the short half-life ($t_{\frac{1}{2}}$, 15m at 15°C). Overall decomposition in the gas phase follows equation (13) with the probable first step as in (14). The thermodynamic properties of the compound have been

$$3BrO_2F \longrightarrow BrF_3 + Br_2 + 3O_2 \qquad (13)$$

$$BrO_2F \longrightarrow BrF + O_2 \qquad (14)$$

calculate by Christe _et al._,[86] whose assignments for the monomer confirm the pyramidal C_s symmetry proposed earlier by Gillespie and Spekkens.[87] In the solid state BrO_2F appears to be associated. It is interesting that the hydrolysis of BrF_5 as well as the reactions of BrF_5 with IO_2F, IOF_3 and I_2O_5 produce BrO_2F but not $BrOF_3$.[87] Krypton(II) fluoride converts BrO_2F initially to $BrOF_3$ and then to BrF_5 : no bromine(VII) species were formed in this reaction.

Bromosyl trifluoride was prepared by the solvolysis of $K[BrOF_4]$ in

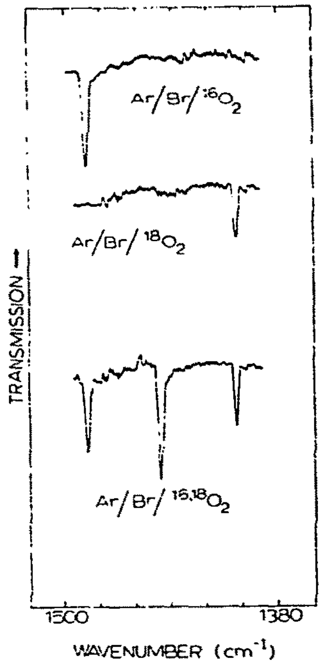


Figure 2. High resolution i.r. spectra of codeposited Ar/Br_2 (discharged) + Ar/O_2 matrix samples at 10K. Top trace depicts a 200:2:1 $Ar/Br/^{16}O_2$ sample; the middle trace shows a 400:4:1 $Ar/Br/^{18}O_2$ sample (99.4% ^{18}O); the bottom trace corresponds to a scrambled oxygen isotopic 100:1:1 $Ar/Br/^{16,18}O_2$ sample (45% ^{18}O).
(Reproduced by permission from J. Am. Chem. Soc., 100 (1978)3955)

anhydrous HF ; $BrOF_3$ appears to be associated in the liquid, solid and solution (in HF) states. Christe et al.[88] have confirmed that association occurs in the liquid and solid states. Their study of the gaseous and matrix-isolated material are consistent with a pseudo trigonal bipyramidal molecule of C_s symmetry with two F atoms at the apices. The results of their force constant calculations show that the equatorial Br-F bond (f_R = 3.51 mdyn/Å) is significicamtly stronger than the two axial bonds (f_R = 2.93 mdyn/Å).

Bromosyl fluoride forms 1:1 adducts with BF_3, AsF_5 and SbF_5 :[89] the Raman and ^{19}F n.m.r. spectra of these adducts have been interpreted in terms of ionic structures containing the $BrOF_2^+$ cation. The cation in the BF_4^- and AsF_6^- salts decomposes to the Br_2^+ ion whereas that in the SbF_6^- salt appears to give BrF_2^+. Christe _et al._[90] have reported improved syntheses for $BrOF_4^-$ as well as IOF_4^- salts and discussed their vibrational spectra.

The reactions of IOF_5 with SbF_5 and AsF_5 have been investigated at low temperature by ^{19}F n.m.r. and Raman spectroscopy.[91] Antimony(V) fluoride forms stable 1:1 and 1:2 complexes whereas AsF_5 forms only a 1:1 complex : the iodine compound binds through its oxygen atom to the Lewis acids AsF_5, SbF_5 and $(SbF_5)_2$. The vapour phase of IO_2F_3 has been studied with the combined techniques of electric deflection and mass spectrometry of a modulated molecular beam :[92] the results indicate that the molecule is essentially dimeric at room temperature and that the dimers begin to decompose at temperatures above 100°C. Although the dimer is non-polar, and, therefore, must be symmetrical the monomer has a polar structure. No evidence for trimeric molecules was found. X-ray crystallographic work by Smart[93] shows conclusively that the dimeric unit existing in the solid state is centrosymmetric. Spectroscopic studies of the adducts of IO_2F_3 with MF_5, M=As, Sb, I, Nb or Ta, and with IOF_3 have shown them to be O-bridged polymers of the type $(IO_2F_4.MF_4)_n$ and $(IO_2F_4.IOF_2)_m$, respectively.[94] The same workers have reinvestigated the reaction between KIO_4 and IF_5; the product $KIO_4.IF_5$ was shown to be a mixture of KIO_2F_4 and IO_2F. They also isolated $KIO_4.2IF_5$ and, hence, pure _trans_-KIO_2F_4; in IF_5 the _trans_ anion isomerizes to a mixture of _cis_ and _trans_ isomers.

The crystal structure of $Al(IO_3)_3.2HIO_3.6H_2O$ has been solved by X-ray methods and can be formulated as $[Al(H_2O)_6][IO_3]_2[HIO_2F_6].HIO_3$: thermal decomposition of this phase occurs at 340°C yielding anhydrous aluminium iodate.[95] A broad line proton magnetic resonance study of HIO_3 and $HIO_3.H_2O$ at -190° and +20°C is consistent with the view that water molecules in the hydrate are incorporated in cavities in the HIO_3 lattice : the n.m.r. line width and second moment of such water molecules is different from the values observed for inorganic hydrates and the oxonium ion and resembles those in ice and clathrate compounds.[96] The crystal structure of $Na(H_3O)[I(OH)_3O_3]$, which is pyroelectric at room temperature, contains the octahedral $[I(OH)_3C_3]^{2-}$ ion with I-O distances of 1.844(2)Å and I-O(H) of 1.920(2)Å.[97] Strong H-bonds, O···H-O 2.544(1)Å, connect oxonium ions to the anion in sheets normal to the polar axis. The application of optical second harmonic generation to the problem of the iodine coordination in hydrated sodium periodate has shown that the salt should be formulated as $Na(H_3O)[IO_3(OH)_3]$.[98] This is in agreement with Poulet and Mathieu's interpretation of the Raman spectrum.[99]

7.1.5 Hydrogen Halides

Dramatic energy shifts in the appearance potential curves for the HF^+ ion have been observed by Foner and Hudson;[100] these are clearly attributable to the production of vibrationally excited HF molecules in the reactions under study, (15) and (16). The proton affinity of HF has been redetermined in the course of a photoionization study of

$$F^{\cdot} + i\text{-}C_4H_{10} \longrightarrow HF + t\text{-}C_4H_9^{\cdot} \qquad (15)$$

$$F^{\cdot} + NH_3 \longrightarrow HF + NH_2^{\cdot} \qquad (16)$$

$(HF)_2$.[101] The new value, 94.3±1.4 kcal mol^{-1}. is significantly less than that, 112±2 kcal mol^{-1}, reported in 1975. An intermolecular potential function for $(HF)_2$, determined from quantum mechanical calculations, has been used in Monte Carlo simulations of liquid HF.[102] Thermodynamic properties, internal energy, energy of vaporisation, heat capacity and dielectric constant at 0^oC were calculated and compared with the available experimental data. An analysis of the inelastic scattering of neutrons from HF in condensed phases has shown that a dominant feature in the data can be explained in terms of two out-of-plane H atom modes.[103] O'Donnell and Peel[104] have developed simple equipment for the determination of vapour pressure of solutions in anhydrous HF. The molal lowering of the vapour pressure at 0^oC was found to be 24.2mm Hg. Solutions of NaF 2,4-dinitrotoluene behaved ideally, however the weaker protonic base 2,4-dinitrofluorobenzene gave approximately 1.5 times the depression expected for a non-electrolyte.

An inexpensive source of dilute HF (0.001-0.3mm Hg) in an appropriate carrier gas has been described:[105] it is based on equilibrium (17) and

$$NaHF_2 \rightleftharpoons NaF + HF \quad (17)$$

on its temperature dependence over the range 60-135°C. The adsorption of HF by anhydrous CrF_3 has been studied by gas adsorption chromatography.[106] The isotherms were found to be non-linear with an isosteric heat of adsorption, which increased with increasing coverage (∤10%). A two-site heteroenergetic surface model was proposed for the system.

Ault[107] has assigned the ν_3 and ν_2 modes of HF_2^- in an Ar-matrix as 1364(970) cm^{-1} and 1217(880) cm^{-1}, respectively (data for DF_2^- in parentheses). He concluded that the shape of the ν_3 band is consistent with a broad centrosymmetric potential energy minimum for the hydrogen. The same author[108] has attempted the synthesis of the neutral free radicals FHF and FHCl by the photolysis of F_2 in the presence of either HF or HCl. I.r. spectra of the resulting Ar matrices gave evidence for the formation of a weakly bound complex between HF and Cl, but none for HF_2. The structure of the H-bonded complex HF-HCl has been determined by molecular beam electric resonance spectroscopy.[109] The complex, a slightly asymmetric prolate top has the H-on-Cl colinear with the two halogens and the H···F distance is 2.12Å. The H-on-F is 50° off the halogen axis.

In the Raman spectra of supersaturated aqueous solutions of the higher hydrogen halides a broad, strongly asymmetric band appears centering on 2600 or 2320 cm^{-1} for HCl and HBr respectively.[110] These bands have been assigned by Giguere et al. to $H_2O\cdots HX$ complexes. In aqueous hydrofluoric acid the nature of the complex is uncertain but the H-bonds are stronger than in the three other HX acids. Dimethylsulphoxide, which is known to suppress proton exchange in alcohol solutions, forms a 1:1 complex with HCl.[111] This complex, m.p. 56-57°C, has been characterized by analysis, ^1H and ^{13}C n.m.r. spectroscopy. Rather unexpectedly, it reacts with CH_2Cl_2 to form $MeSCH_2Cl$, presumably via Me_2SCl_2 as intermediate.

The i.r. absorptions of MnO_3F in an Ar matrix containing 0.5% HF display satellite bands, which were attributed to complexes between MnO_3F and HF.[112] On the other hand, gaseous MnO_3F is converted by HCl to MnO_3Cl, which could be identified by i.r. spectroscopy. Sulphur(IV) fluoride has been found to react with anhydrous HX, X=Cl, Br, or I, at -78°C in CCl_3F to form the free halogen as well as SCl_2, S_2Br_2, or SI_2, which decomposes above -40°C.[113] Although sulphuryl fluoride, SO_2F_2, does not react with anhydrous HI, sulphuryl chloride fluoride is reduced to H_2S, HCl, HF, H_2O and I_2.[114]

Coulombean et al.[115] have used ^{19}F n.m.r. spectroscopy to determine the equilibrium constants for the ionization and association processes of HF in formic acid (see below), presumably at room temperature. The enthalpies of solution of LiF, NaF, and KF at 298K in aqueous HF have

$$
\begin{array}{ccc}
H^+,\ F^-,\ HF & \underset{K_1=1.1\times10^{-5}M}{\rightleftharpoons} & HF,\ HF \\
K_D=0.5M\ \Big\updownarrow & & \Big\updownarrow\ K_D'=0.5M \\
H^+,\ HF_2^- & \underset{K_1'=1.1\times10^{-5}M}{\rightleftharpoons} & H_2F_2
\end{array}
$$

been measured for acid concentrations up to 28.3M.[116] The enthalpy of solution of LiF does not show a maximum value at about 1.5M HF unlike the corresponding enthalpies of NaF and KF. Equations for the kinetics of solution of quartz in aqueous HF or aqueous NH_4HF_2 have been reported.[117] At equal concentrations of fluoride NH_4HF_2 reacts 1.5 times faster than hydrofluoric acid. Bessiere and Pillet[118] have investigated the use of LaF_3 and Si to monitor F^- ion activities in H_2O-H_2SO_4-HF mixtures (H_2SO_4, 15 to 26N; HF, 0 to 3M).

In a study of the M_2SnF_6-HF-H_2O, M=K or Na, system at 0^oC, $M_2SnF_6.4HF$ are formed at high HF concentrations whereas Na_2SnF_6 or $K_2SnF_6.n(H_2O).(1-n)HF$, $n \leq 1$, are formed at lower concentrations.[119] Isothermal solubility studies of the SbF_3-HF-H_2O system at 0^oC[120] have shown that the solid phases in equilibrium are $SbF_3.0{\cdot}5H_2O$, SbF_3 and $SbF_3.HF$. The BiF_3 system is analogous except that the hydrated phase is the monohydrate.[121] Studies of a number of ternary systems HF-H_2O-organic solvent have established that HF is the poorest homogenizing agent for H_2O-i-C_4H_9OH mixtures of the hydrohalic acids.[122] A solubility study at 25^oC of KF in HF-dimethylsulphoxide and in HF-acetic acid has shown that the only solvated species produced are KF.nHF (n=1, 2, 2.5, 3 and 4) in both systems:[123] this is the same result as for the KF-HF-H_2O system.

The controlled hydrolysis of PuF_6 in liquid HF has been shown to generate $PuOF_4$ as a brown, involatile solid, which shows a tendency to reproportionate to PuF_6 and PuO_2F_2.[124] ^{75}As n.m.r. spectroscopy of the AsH_4^+ ion has confirmed that this ion is stable in liquid HF.[125] The silver electrode has been used to follow reactions of silver salts in HF such as complex formation with ligands such as PH_3, AsH_3, HCN, CO and PF_3.[126] In the presence of AgCl and HCl it functions as a fluoride ion electrode. Devynck *et al.*[127] have reported that the same electrode system operates reversibly even in the superacid medium HF-SbF_5 at SbF_5 concentrations up to 60 wt. %.

Salts of closo-decahydrodecaborate(2-) react with anhydrous HF at or below room temperature to give complex mixtures of high molecular weight (e.g. 450, 630 and 2300) boranes.[128] Salts of $B_{12}H_{12}^{2-}$ and $B_{10}Cl_{10}^{2-}$ do not react under the same conditions. The enthalpies of formation (all in kcal mol^{-1}) of the 1:1 complexes of HF with furan (-4.8), tetrahydrofuran (-7.36), 2,5-dimethylfuran(-6.7), and 2,5-dimethyltetrahydrofuran(-7.4) have been determined by precision calorimetry.[129] Moreover the frequency shifts, $\Delta\nu$(HF), on hydrogen bond formation were obtained by i.r. spectroscopy. *Ab initio* MO calculations were also carried out for the 1:1 complexes HF.furan and HF.tetrahydrofuran and were found to agree with the trend of the experimental data.

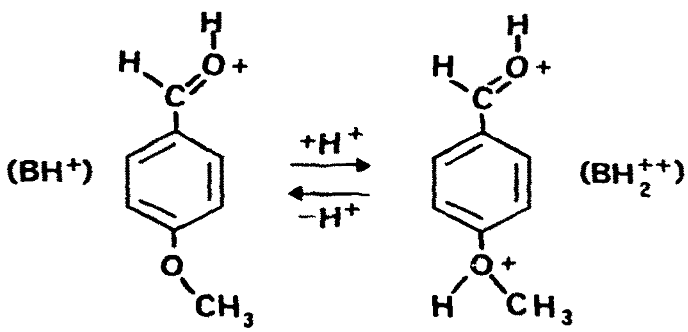
MacLeod and O'Donnell[130] have investigated the polarography of the p-block elements In(III), Tl(I), Pb(II), Cd(II), As(III), Sb(III), Bi(III) as well as of the hydrogen halides in anhydrous HF using a dropping mercury electrode. A high degree of irreversibility was detected for many of these systems especially in the presence of added F^- ion : these workers state that AsF_5 and SbF_5 cannot be present because they are too strongly oxidising. By contrast Devynck *et al.*[131] report that very dilute solutions of SbF_5 in HF containing KF (0.2M) are not electroactive. Solutions of $SbCl_5$ under the same conditions are active although as HCl is lost from the system the activity diminishes. The same workers also examined the polarographic behaviour of SbF_3 in aqueous and anhydrous HF.[131]

According to Serushkin *et al.*[132] electrochemical oxidation of H_2O(1 and 5.5M) at a Ni anode in liquid HF takes place at a potential 1 to 1.5v lower than that for F^- discharge : at this potential the only anodic electrolysis product is O_2, i.e. O_3 and F_2O are not formed. Clarke and Kuhn have reported on fluorination of the model compound $MeSO_2F$ in HF and on fluorine evolution at nickel in this medium.[133] Electrochemical oxidation of fluorobenzenes and octafluoronaphthalene in HF has been investigated. The half-wave potentials were found to be independent of both KF and SbF_5 concentrations : the evidence was said to be consistent with the formation of stable cation radicals.[134] Anodic displacement of Br by F has been accomplished electrochemically in HF for 1,2-dibromoethane and -propane.[135] The anodisation of aluminium in liquid HF containing small amounts (<10%)

of water produces an anodic coating of fluorides and oxides : rapid corrosion of Al was found to occur at higher concentrations of water.[136]

I.r. spectra of the solid 1:1:1 complex between fluoroacetone, HF and SbF_5 are consistent with the formulation, $(Me\overset{+}{C}(OH)\cdot CH_2F)(SbF_6^-)$.[137] Perylene is oxidised in HF to the radical cation; the reversible electrochemical oxidation of this radical cation is not a function of the fluoride ion activity.[138] Herlem and Thiebault have used this behaviour to measure the acidity function values, R(H), at 0^oC for solutions containing 1M NaF and a mixture of BF_3 and BF_4^-. The hydrogen and chloranil electrodes in HF have been used to set up a complete potential-pH diagram.[139] The same workers were also able to revise the autoprotolysis constant for anhydrous HF, $K=[H^+][F^-] = 10^{-13.7}$ $mol^2\ l^{-2}$.

Sommer et al.[140] have used ^{13}C n.m.r. spectroscopy to determine the relative concentrations of mono- and di-protonated p-methoxybenzaldehyde (BH^+) and (BH_2^{2+}), respectively,in the two super-acid media $HF-SbF_5$ and HSO_3F-SbF_5. Their results suggest that 2 mol% SbF_5 in HF is as acidic as 15 mol% SbF_5 in HSO_3F and also that 4 mol% SbF_5 in HF is 10^3x more acidic than 4 mol% SbF_5 in HSO_3F.



Siskin[141] has investigated the interaction of solutions of TaF_5 in HF at 50^oC with several cycloalkanes in the presence of H_2 (200 psi). The catalytic reactions commence with rapid isomerization and are followed by ring cleavage/hydrogenolysis. Tantalum(V) fluoride is used in preference to SbF_5 in these studies because it is not reduced by H_2. Bonifay _et al_.[142] have, however, examined the kinetics of isomerization of n-pentane and n-hexane in the $HF-SbF_5-H_2$ system.

7.2 HYDROGEN

A report concerned with the radiological hazard arising from exposure to either gaseous T_2O or T_2 concludes that the former is 10^4x more hazardous.[143] The hydrogenolysis, equation (18), of a series of alkylcaesiums, CsR, has been studied spectrophotometrically in

$$CsR + H_2 \rightleftharpoons RH + CsH \quad (18)$$

cyclohexylamine.[144] The caesium salt of p-phenyltoluene (PPT) reacts completely with H_2 (1 atm., room temperature), whereas the salts of di-2,4-xylylmethane (DXM) and of diphenylmethane (DPM) are unreactive: thus the pK_a value of H_2 appears to be intermediate between that of PPT (38.7) and those of DXM (36.3) and DPM (33.1). The series of equilibria represented by (19) has been measured for (n, n+1); n=1 to 5

$$H^+(H_2S)_n + H_2S \rightleftharpoons H^+(H_2S)_{n+1} \quad (19)$$

in a pulsed electron beam mass spectrometer.[145] The addition of water vapour was shown to produce mixed cluster ions, such as $H^+(H_2S)_x(H_2O)_y$ with (x + y) ranging from 1 to 6 : the temperature dependence of some of the equilibria involving such mixed cluster ions were obtained and it was shown that the hydration process is energetically more favourable than solvation by H_2S.

Additional evidence has been published by Nagyrevi and Sandorfy[146] of the influence anaesthetic agents may exert on hydrogen bonding equilibria involving water molecules : they reported the i.r. spectra of a 0.04M solution of water in a glass of 2-methyltetrahydrofuran at -190^oC in the presence of $CHCl_3$, CF_3-CHClBr as well as tetramethylurea.

Ichikawa[147] has analysed the results of recent, accurate crystal structure investigations and has re-examined the correlation between O-H and O···O distances in OHO H-bonds. The average correlation curve of asymmetric bonds appears to coincide with that of symmetric bonds only at the lower limit of O···O length (2.4Å) (Figure 3). On deuteration an expansion of up to 0.027Å may occur. A report of a very short, asymmetric H-bond (O-H, 1.09); O···O, 2.477(2)Å has been

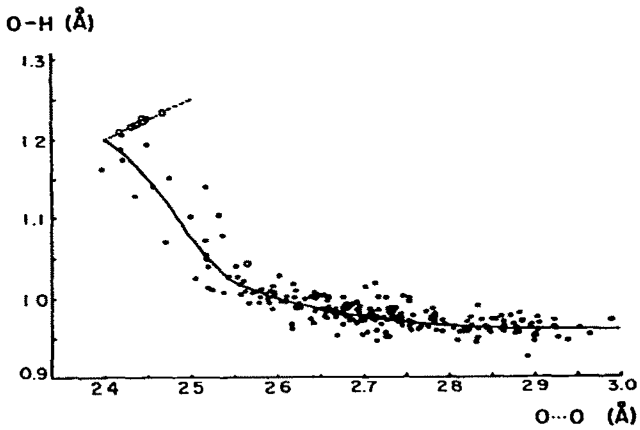


Figure 3. A diagram of the correlation between O-H and O···O distances in OHO H-bonds. Open circle : symmetric; filled circle : asymmetric H-bond. (Reproduced by permission from Acta Crystallogr., B34(1978)2074.)

made by Harlow and Shelton[148] on the basis of an X-ray study of diprotonated 1,5-dimethyl-1,5-naphthyridine-4(1H),8(5H)-dione trifluoroacetate at $-35^{o}C$.

The crystal structures of deuterated formic[149] and acetic[150] acids at temperatures less than 20K have been refined using neutron powder diffractometry. The resulting geometry of formic acid differs somewhat from that reported in 1953 ; the C-O bond lengths are now in reasonable agreement with those of other carboxylic acids. The CD_3COOD structure is essentially the same as that reported earlier for the protio compound.

The asymmetric environment of the oxonium ion in the trifluoromethanesulphonate salt has been re-investigated in a neutron diffraction study by Lundgren et. al.[151] The O-H···O distances range from 2.522 to 2.673Å and the H-bonds are bent with angles at H from

162.0 to 170.7(4)^{o}. Although the OOO angles are very different (see Figure 4), the three HOH angles are in better agreement with an idealized C_{3v} symmetry. The pentahydrate of trifluoromethanesulphonic

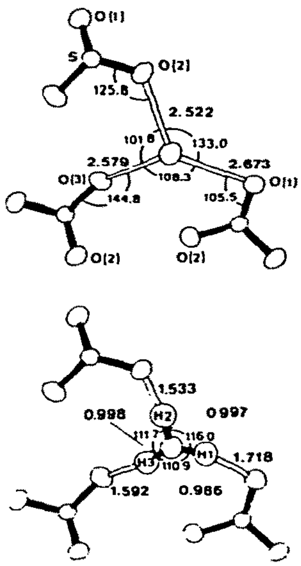


Figure 4. Geometry of H_3O^+ and its environment in $H_3O^+CF_3SO_3^-$. (Reproduced by permission from Acta Crystallogr., B34(1978)2945.)

acid has a structure (at 90K) which can be best described as $[H_3O^+][CF_3SO_3^-].4H_2O$.[152] The oxonium ion is H-bonded to 3 water molecules, O···O distances 2.482, 2.579 and 2.639Å, so that it could be described alternatively as $H_9O_4^+$. At 95K the tetrahydrate contains the triaquaoxonium ion, $H_9O_4^+$, H-bonded to the anions : the average O···O distances are 2.54Å.[153] X-ray diffraction methods have yielded the structure of $HCl.6H_2O$ at 87K.[154] This structure also contains the $H_9O_4^+$ ion, which is linked to H_2O molecules H-bonded to one another and to Cl^- ions to form a larger structure.

Westrum et al.[155] has determined the heat capacities of $RbHF_2$ and $CsHF_2$ by adiabatic calorimetry over the temperature range 300 to 530K. The data for the rubidium salt are comparable to those for the isostructural potassium salt. An additional solid-solid phase transition was noted for the caesium salt. ^{1}H and ^{19}F n.m.r. spectra of $K_2SnF_6.4HF$ and $Cs_2MF_6.4HF$, M = Sn or Ge, have been said[156] to confirm that the HF molecules are coordinated to the octahedral anions, MF_6^{2-}.

The geometrical characteristics of O-H···F bonds in $MF_n.xH_2O$ have been reviewed by Simonov and Bukvetsky.[157] The average O···F distance is 2.682Å and all known bonds lie in the range 2.56 to 2.86Å. An X-ray structure determination of $[Cr(H_2O)_6]F_3.3H_2O$ has shown that the three F^- ions and three H_2O molecules are H-bonded together (O-H···F, 2.61 to 2.65Å) and to the octahedrally hydrated chromium ions (O-H···O, 2.55 to 2.61Å).[158] The addition of F^-, in the form of NBu_4F or KF.18-crown-6, to solutions of ß-diketones in MeCN causes the OH resonance to shift upfield : this observation has been attributed to strong H-bonding between the enol form and F^-.[159] Clarke has estimated that the $\delta(O-H\cdots F^-)$ proton chemical shift of the 1:1 complex is ca. 13 p.p.m. upfield from that of the pure enol.

Tetraethylammonium chloride monohydrate has a structure in the solid state in which pairs of Cl^- ions and H_2O molecules form a centrosymmetric H-bonded ring.[160] An X-ray structure analysis of $[RR'PCl_2^+][HCl_2^-]$, R = 4-$MeOC_6H_4$, R' = Me, has shown that the anion is bent, ClHCl angle 168°, and is asymmetric, H-Cl distances 1.45 and 1.78Å.[161] The preparation of the tetra-n-butylammonium salts of the new anions, $ClHCN^-$ and $BrHCN^-$, have been reported.[162] The i.r. spectra of the protio and deutero compounds were discussed. The dimeric structure of $[CdI_2(HN:PPh_3)_2]_2$ arises from N-H···I interactions, where the N····I distance is 3.76Å.[163]

High resolution ^{19}F n.m.r. spectra have been reported for the superacid systems $HSO_3R_f.nSbF_5$ (n=0 to 5; R_f=F, CF_3 or C_2F_5) at -40° or -60°C.[164] The SbF_5 group retains the usual cis-polymeric configuration in these compounds.

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