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Chapter 7

THE HALOGENS AND HYDROGEN

M.F.A.Dove

7.1 THE HALOGENS

7.1.1 The Elements

A recent paper by Dreyer et al.[1] summarises what little work has been published on the chemistry of astatine: their own contribution is to remeasure the ionic mobility of At^- in alkaline, acidic and neutral aqueous solution. In the presence of other halide ions they have inferred that AtY_2^-, X = Cl, Br or I, are generated as a result of reaction with atmospheric oxygen. The relative electronegativities of F and $OTeF_5$ have been reinvestigated by Birchall et al.[2] Using ^{129}Xe and ^{125}Te n.m.r. as well as ^{129}Xe and ^{127}I Mössbauer spectroscopy they have re-affirmed their proposal that F is the more electronegative group; on the Pauling scale they have assigned a value of 3.87 for the electronegativity of $OTeF_5$. The low-temperature fluorination of $M_2(Me)_6$, M = Si or Ge, with F_2 leads in both instances to M-M bond cleavage.[3]

Woolf[4] has reviewed the thermochemistry of inorganic fluorine compounds and an international group[5] have investigated a number of

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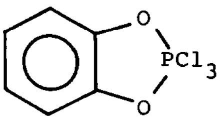
NF_4^+ compunds. Their estimate of the enthalpy of reaction (1), +36(±40) kJ mol^{-1}, is clearly consistent with past failures to

$$NF_3(g) + F_2(g) \rightarrow NF_4^+F^-(s) \qquad \ldots(1)$$

synthesise $NF_4^+F^-$.

Chlorine free radicals have been produced homogeneously in a flow reactor by the i.r. multiple-photon-induced decomposition of CF_2Cl_2 or PhCl.[6] The observation that gold, palladium and platinum catalyse the formation of phosgene from CO and Cl_2 in the dark at atmospheric pressure and room temperature is said to be consistent with the formation of halometal carbonyls as intermediates.[7] Up to 60mol $COCl_2$ were produced per mol of gold.

The reactions of chloramine with NH_2·CS·SMe and MeNH·CS·SMe have been reported:[8] chloramine appears to function as a simple oxidiser, behaving analogously to t-BuOCl in the reaction with NH_2·CS·SMe. Gloede[9] has summarised the chemistry of brenzcatechylphosphorus trichloride (1) and of brenzcatechylphosphorus oxide chloride (2) as chlorine transfer agents.



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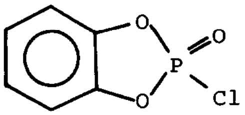


(2)

An excited state photoelectrochemical cell has been designed in which H_2O_2 and Br_2 are separately produced in MeCN solution with high efficiency.[10] The net cell reaction (2) has ΔE^o of +0.4V.

$$O_2 + 2H^+ + 2Br^- \rightarrow H_2O_2 + Br_2 \qquad \ldots(2)$$

Efficient and regiospecific bromination of activated aromatic compounds is effected by hexabromocyclopentadiene in a process which is interpreted as involving formation of Br^+ and $C_5Br_5^-$.[11] The reaction of an aryltin(IV) compound with ammonium $[^{82}Br]$-bromide, chloramine-T, and HCl in EtOH-H_2O at 0^oC leads to rapid cleavage of the aryltin bond and formation of the labelled aryl bromide.[12] Carrier-free radiobromodestannylations have also been reported.[13]

The spectrophotometric properties of the contact charge-transfer complexes of I_2 with saturated hydrocarbon solvents, e.g. cyclohexane and heptane, have been calculated from the UV spectra.[14] Iodine complexes (1:1) with hexamethylborazine, $B_3N_3(Me)_6$, and 10-methyl-10,9-borazarophenanthrene have been detected in CCl_4.[15] The solutions of $B_3N_3(Me)_6$ with I_2 are unstable and deposit a white solid. The iodine adducts of 6-nylon have been shown to act as cathodes of aqueous galvanic cells;[16] for example, the e.m.f. of such an electrode with a Zn anode is 1.4V at 25°C. Measurements on electrochemical cells of the type $Pt|I_2$, KI in py$||I_2$ in py$|Pt$ in conjunction with electrical conductivity measurements have been used to study ionic equilibria in 0.16 to 1.6M solutions of I_2 in pyridine (py);[17] the results were discussed in terms of an ionisation mechanism of the 1:1 complex. Spectroscopic evidence has been reported for the association of I_2 with one pyridyl ring in some bis-pyridyl substituted ethenes and ethynes:[18] with excess I_2 other products, very insoluble in CH_2Cl_2, were formed. The complex formed between 2,2'-bipyridyl and I_2 has been shown to have 1:1 stoichiometry and the thermodynamics of complex formation have been calculated.[19]

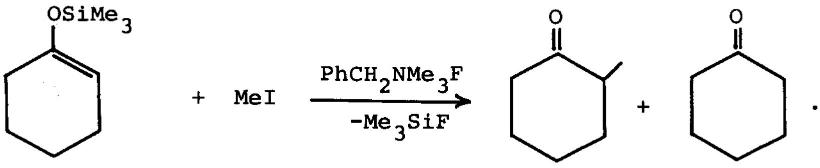
7.1.2 Halides

Fluoride is rarely encountered as a ligand in organometallic compounds. Grundy and coworkers[20] have now reported that $ReH_2(NO)(PPh_3)_3$ reacts with HBF_4 or HPF_6 in the presence of CO to give the novel formation $[ReF(CO)(NO)(PPh_3)_3]^+$, which, with certain coordinating anions, X^-, gives $[XReF(CO)(NO)(PPh_3)_2]$. Although the nephelauxetic parameter for F^- is usually assigned a value of 0.8, higher values (up to 1.38 for Tl^+) have been derived for the main group cations Tl^+, Pb^{2+}, and Bi^{2+} in molten (Li,Na,K)F from the UV spectra of their solutions.[21] Moreover the addition of KF to molten alkali metal tetrafluoroborates containing these ions leads to gradual replacement of the polarised fluorines of the fluoroanion. Interesting examples of compounds having F bridging a transition metal and silicon have been synthesised by Reedijk et al.[22] The addition of N-vinylimidazole, viz, to alcoholic solutions of $MSiF_6$, M(II) = Mn, Fe, Co, Ni, Cu, or Zn, produced $M(viz)_4SiF_6$: the crystal structure of the Co(II) complex shows trans F-bridging by the SiF_6 group of $Co(viz)_4$ units.

The fluoroformate anion, FCO_2^-, has been isolated for the first time in a condensed-phase synthesis.[23] Caesium fluoride vapourised at 500°C and codeposited with Ar/CO_2, 1000:1, showed i.r. absorptions at 883 cm^{-1}, ν(CF), 1316 and 1749 cm^{-1}, ν(CO). On the basis of the observed isotopic shifts as well as semi-empirical CNDO/2 calculations the planar C_{2v} structure is favoured over the C_s structure.

The crystal structures of $KF.(CH_2)_n(CO_2H)_2$, n = 1[24] and 2,[25] have been determined by Emsley and colleagues. Both compounds have chains of the dicarboxylic acid molecules hydrogen bonded to fluoride ions. The authors discussed the extent to which structures of the type $[\bar{O}_2C(CH_2)_nCO_2H\cdots F\text{-}H\cdot\cdot]_x$ contribute to the net structure. Ab initio calculations have shown that a uracil-fluoride ion complex is thermodynamically stable even when hydrated.[26] The implications of this finding for nucleic acid biochemistry were briefly discussed. Multinuclear (^1H, ^{19}F and ^{15}N) magnetic resonance studies are consistent with the formation of H-bonds by F^- with the N(1)-H site.[27] Thermal decomposition of the complex occurs via HF_2^-, uracil anion and neutral uracil.

Treatment of enol silyl ethers (3) with alkyl halides in the presence of $PhCH_2NMe_3^+F^-$ and molecular sieves at room temperature gives the corresponding monoalkylated products with high regiospecificity.[28] In the absence of the molecular sieve, reaction (3) yields the proton transfer product, cyclohexanone,



..(3)

(3) (4)

rather than the methylated product (4). The conditions for pre-drying $PhCH_2NMe_3F$ were fully reported. Wasserman and Pickett[29] report "a remarkable fluoride ion effect" taking place in the reactions of a series of enolic compounds, e.g. α- and β-diketones, with singlet oxygen. In the absence of F^- dye-sensitised photo-oxidation proceeds very sluggishly in these systems: however, in the presence of F^- the reactions are complete within a few hours yielding ketonic products and other derivatives resulting from α-hydroperoxide formation.

Fluorine magnetic resonance spectra of solutions of KF-18-crown-6 in a variety of organic solvents show linewidths, ca. 6kHz, essentially indistinguishable from those of solid KF:[30] this evidence is consistent with the presence of tight ion pairs or higher aggregates in solution. Catalysis by such solution of the Michael addition reaction between nitroalkanes and enones forms the basis of some syntheses of a variety of 1,4-diketones.[31]

The anion exchange equilibria in water and in MeOH have been measured to obtain thermodynamic equilibrium constants.[32] The ionic selectivity sequence $I^- > NO_3^- > Br^- > Cl^-$ obtains in both media. Calculations using the available values of ionic free energies of transfer were in good agreement with experiment and allowed the authors to rationalise the reversals in selectivity in DMSO of Cl^- and Br^- against I^-. An anion exchange method for the determination of chloride, bromide, and iodide has been described.[33] The detection system employs an anion-sensitive microelectrode based on silver. The kinetics of the oxidation of I^- by Cu(II) has been studied in acidic solution, in the presence of excess Cl^- to render CuI soluble.[34]

7.1.3 Interhalogens and Related Species

The reaction of ClF and SF_4 in the gas phase under conditions of isotopically selective (laser) photochemical excitation yields either SF_5Cl or S_2F_{10} and Cl_2:[35] on this basis the authors have proposed a kinetic model. In cryogenic solutions CW laser irradiation has permitted the observation of radical species such as $ClF_2\cdot$. The reaction mixture Cl_2-HgF_2 effects the addition of ClF to N≡S- and N≡C- centres;[36] similarly Br_2-HgF_2 mixtures caused the addition of BrF to $N{\equiv}C{-}R_f$ substrates. Nazarov and Antimonov[37] have examined the products of thermal decomposition of $C_4F.0.46ClF_3$ by ^{19}F n.m.r. spectroscopy, whereas another study of ClF_3- and BrF_3-graphite compounds has employed mass spectrometry.[38] Habibi and Sams[39] have claimed to have synthesised perfluoro-n-heptylbromine(V) tetrafluoride by the reaction of n-$C_7F_{15}Br$ and F_2 at 0^oC. Although the new compound decomposes slowly at room temperature it could be purified by gas chromatography with a column temperature of 100^oC.

The tribromide, Br_3^-, salt of Ph_4P^+ has been shown to be isomorphous with one of the two polymorphs of the arsonium analogue;[40] the Br_3^- ion is centrosymmetric. Harris and McKechnie[41] have re-examined the stability of the caesium trihalides by measurement of dissociation pressures (DP) and by comparison of procedural decomposition temperatures (TGA). The relative stabilities as determined by the two methods yield two different series. Neither series agrees with that reported by

DP.....$IBr_2^- > I_3^- > ICl_2^- > Br_3^- > I_2Br^-$

TGA....$ICl_2^- > IBr_2^- > I_3^- > I_2Br^- > Br_3^-$

Ephraim in 1917. It was pointed out that the TGA method is significantly affected by kinetic factors.

The reaction of I_2^+ and selenium in liquid SO_2 has been shown to generate the $Se_2I_4^{2+}$ ion, equation (4).[42] The structure of the

$$2I_2Sb_2F_{11} + 2Se \xrightarrow{SO_2} Se_2I_4(Sb_2F_{11})_2 \qquad ...(4)$$

new cation was shown to be similar to the eclipsed dithionite ion. The ^{127}I Mössbauer spectra of some chalcogen-iodine cations have been recorded.[43] The data indicate that the nature of the chalcogen-iodine bond is essentially p in character. Birchall and Myers[44] have shown by ^{127}I Mössbauer spectroscopy that the I_2^+ ion dimerises in HSO_3F at low temperatures; this process can now more safely be linked to the previously noticed colour changes, from intense blue to red-brown, on cooling.

The electronic structures of long polyiodide chains have been investigated.[45] The results permit a rationalisation of bond lengths and bond angles. Consideration of the electronic properties indicated where fresh experimental evidence might be valuable. A mixture of dithizone and iodine (1:4) refluxed in $CHCl_3$ gives black needles of composition 2dithizone.$7I_2$ on cooling.[46] The product (5) is a centrosymmetric molecule which contains non-planar $(I_2)_5$ chains anchored at both ends by sulphur. The phase diagram of the ternary system SrI_2-I_2-H_2O has shown a single polyiodide, $SrI_{18}.7H_2O$, as well as $SrI_2.7H_2O$, to be the stable solid phases at 0°C.[47] A neutron diffraction study of the polyiodide was said to be in press.

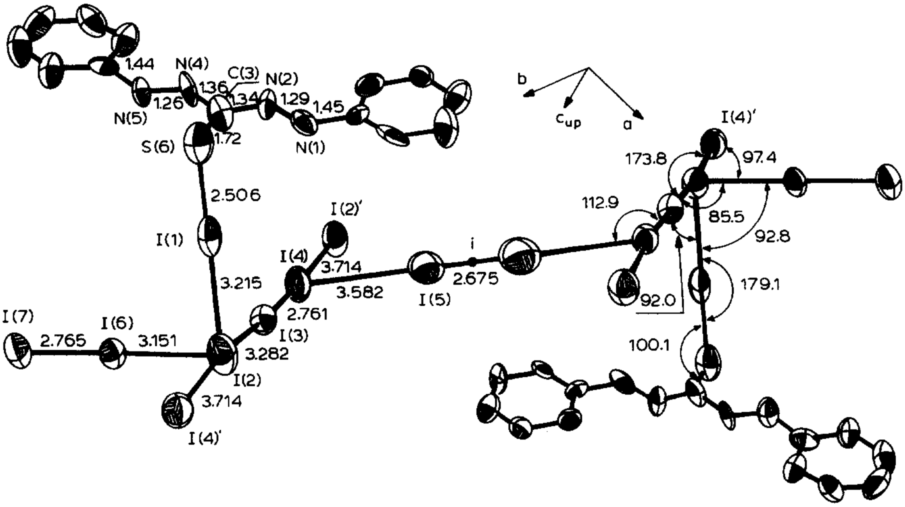


Figure 1. The molecular structure of (5) showing bond lengths (Å) and angles (°). I(2)', I(4)' and the corresponding atoms in the other molecular half belong to neighbouring molecules (reproduced by permission from Angew. Chem. Int. Ed. Engl., 21(1982)219).

The reaction of $[(\eta\text{-}C_5Me_5)M]_2I_n$, M = Rh or Ir, n = 4, with I_2 gives first the compound with n = 6 and then that with n = 8.[48] The structure of the former product has two bridging and two terminal iodine atoms per $[(C_5Me_5)M]_2$ unit of which the terminal iodines are linked via slightly elongated iodine molecules, I-I = 2.787(2)Å, with each other. The products of the alkylation of red phosphorus with alkyl iodides in the presence of I_2 contain polyiodide salts of $R_3PPR_3^{2+}$ cations.[49] Coordinated polyiodide ions are features of the recently reported structures of $[Cu(NH_3)_4I_2.I_2]$, $[Cu(NH_3)_4I_3]I_3$, $[Cd(NH_3)_4I_2.I_2]$ and $[Cd(NH_3)_4(I\text{-}I_2)_2]$.[50] The new compound $[Pd(NH_3)_4]I_8$ has been shown to contain a Z-shaped anion for which the I-I distances suggest the following description $I_3^-.I_2.(I^-I_2)$.[51]

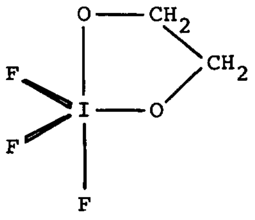
Grushin et al. have reported that the chlorination of 9-iodo-o(m)-carboranes, $9\text{-}C_2H_2B_{10}H_9I$, proceeds quantitatively to form the light-sensitive $9\text{-}C_2H_2B_{10}H_9(ICl_2)$.[52] Further reactions of these compounds to generate the bis-trifluoroacetates and also the phenylcarboranyliodonium salts, and the products of I-Ph cleavage,[53] were described. Birchall and Myers[54] have prepared $I_3Cl_2^+SbCl_6^-$ and characterised it by single crystal X-ray and Raman data. The reactions of $PhI(O_2CR)_2$, R = Me or CF_3, with X_2, X = Cl, Br or I, take place primarily according to equation (5)

$$PhI(O_2CR)_2 + X_2 \rightarrow PhI + 2RCO_2X \qquad ...(5)$$

$$PhI(O_2CR)_2 + PhICl_2 \rightleftharpoons 2PhI + 2RCO_2Cl \qquad ...(6)$$

with the formation of acyl hypohalites.[55] When X = Cl equilibrium (6) is set up involving $PhCl_2$. The dicarboxylates also react with BX_3 and AlX_3 to give similar products although when X = Cl and R = Me chlorination of iodobenzene results. In general it was noted that reactions of the above type can be used to effect brominations or chlorinations of aromatic substrates more reactive than PhI.

Buslaev and coworkers have studied some reactions of IF_5. With 1,2-diols compounds of the type (6) are formed; the monomethyl



(6)

diol yields two isomeric species whereas the 1,2-dimethyl-1,2-diol produces two diastereoisomers.[56] With either Et_3N or Et_2NH in MeCN 1:1 adducts were shown to be formed by ^1H and ^{19}F n.m.r. spectroscopy; both adducts were claimed to be octahedral.[57]

7.1.4 Oxides, Oxide Halides and Oxoanions

The low temperature heat capacity of caesium fluoroxysulphate, $CsSO_4F$, has been determined by adiabatic calorimetry.[58] Using the previously obtained ΔH^o_f value the standard electrode potential of process (7) in water was calculated to be 2.47(±0.01)V.

$$SO_4F^- + 2H^+ + 2e^- \rightarrow HSO_4^- + HF \qquad ...(7)$$

The i.r. and Raman spectra of solid $CsSO_4F$ and $RbSO_4F$ have been measured and compared with the gas phase spectra of the isoelectronic O_3ClOF.[59] The spectra are consistent with a perchloric acid type structure of C_s symmetry. A spectroscopic study of pure ClO_4F, prepared by the thermal decomposition of NF_4ClO_4, has included ^{19}F n.m.r. in HF, and i.r. and Raman for the gas as well as in matrices at 4K.[60] The chlorination of $TeF_5(OH)$ with either $ClOSO_2F$ or ClF furnishes $TeF_5(OCl)$ in high yield.[61]

Reactions of BrO, interesting from the viewpoint of atmospheric chemistry, along with HO_2 have been studied kinetically.[62] The results are close to those predicted by analogy with ClO. The rates of formation of NH_2Br, Me_2NBr, N-bromoglycine and N-bromoglutamate from OBr^- and excess nitrogen compound have been determined in the pH range 7-13.[63] The variation of the observed second order rate constants with pH is consistent with a mechanism in which HOBr and OBr^- react simultaneously with the free base. DuPont workers have reported that Cl_2O is a powerful and selective reagent for either side-chain or ring chlorination of deactivated organic substances;[64] excellent yields under mild conditions were claimed. Their results are consistent with a free radical process involving hydrogen abstraction by the $OCl\cdot$ radical. In the presence of a strong protonic acid ($pK_a \leqslant$ that for CF_3CO_2H)Cl_2O brings about ring chlorination: the intermediate responsible for these reactions may well be a hypohalite, produced in a process like (8). Allylaryliodonium species are claimed to be the

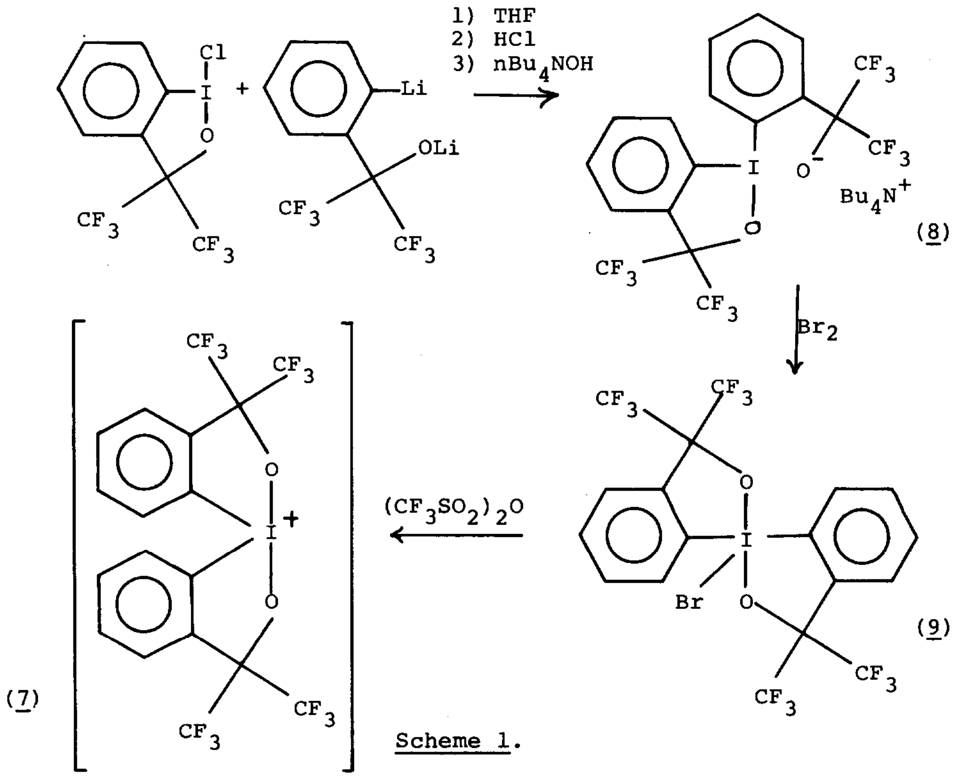
$$Cl_2O + CF_3CO_2H \rightleftharpoons CF_3CO_2Cl + HOCl \qquad ...(8)$$

intermediates formed in the reaction of allylsilanes with iodosylbenzene, PhIO, in the presence of $BF_3.Et_2O$.[65] The stoichiometry of the reaction between ClO_2^- and I_2 in the pH range 2 to 5 and at low I^- ion concentrations has been found to correspond to equation (9).[66] The kinetics are said to be

$$5ClO_2^- + 2I_2 + 2H_2O \rightarrow 5Cl^- + 4IO_3^- + 4H^+ \qquad ...(9)$$

compatible with a mechanism in which $IClO_2$ is the key intermediate.

Gaseous chlorine perchlorate, $ClOClO_3$, has been shown to be a major photolysis product of ClO_2.[67] The technique of time-resolved i.r. spectral photography (TRISP) was used to monitor the growth of its characteristically strong 1282 cm^{-1} band. Scheme 1 outlines the synthesis of a stable pseudo-trigonal bipyramidal 10-I-4 organoiodine cation, (7), as its triflate salt.[68] Compound

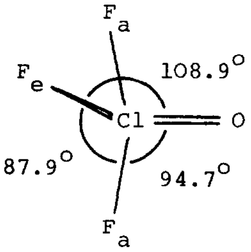


Scheme 1.

(8) was thought to be a bicyclic 12-I-4 species, however its ^{19}F n.m.r. spectrum indicates that the anion is unsymmetrical. Compound (9), a bromoperiodinane, provides the first example of a

compound with a bond joining bromine to iodine(V); this compound is indefinitely stable at room temperature and is inert to atmospheric moisture, however it brominates THF or MeCN to re-form (8).

The structure of gaseous ClF_3O has been determined by electron diffraction by Oberhammer and Christe.[69] The axial F-Cl (1.713Å) bonds are significantly longer than that of the equat. F-Cl (1.603Å) bond and of the O=Cl (1.405Å) in the C_s symmetry molecule. The angular distortions arising from the lone pair in the trigonal bipyramidal coordination sphere are shown below. The angles in the equatorial plane subtended at Cl by the lone pair and F_e (116°) and O (135°) were derived by ab initio calculations.



A structural model of water, into which XO_3^-, X = Cl, Br, or I, ions are introduced, has been described by Lyashchenko et al;[70] they discussed the underlying reasons for the different physicochemical properties of the solution and report measurements of dielectric and electrical conductivity properties of solutions of $KBrO_3$ and KIO_3. Pascal and coworkers[71] have reported that zinc metal is converted by Cl_2O_6 to $ClO_2[Zn(ClO_4)_3]$, which decomposes in vacuo at 67°C to give $Zn(ClO_4)_2$. The new bridging perchlorate complexes $Sb_8Cl_{24}O_5(ClO_4)_6$ and $Sb_2Cl_6(OH)(O)(ClO_4)$ have been obtained by the reactions of $SbCl_5$ with Cl_2O_6:[72] the structure of the latter compound was shown by X-ray crystallography to be a dimeric trichloroantimony(V) oxide stabilised through protonation by perchloric acid. A discussion of the factors involved in the explosion of a (thermally) partially dehydrated sample of Co(II) perchlorate should be read by other workers in this field.[73]

The primary photolysis (185nm) products of $KClO_4$ have been shown to be O_2 and ClO_3^-:[74] the dominant secondary product is Cl^-. It was proposed that the primary photolytic process is photoionisation in which an electron is transferred between adjacent anions. The resulting charge-transfer complex may be responsible for the transient optical absorption. The reaction of $NH_3O\overset{+}{H}ClO_4^-$ with $CaCO_3$ in a 3:1 ratio yields a mixture of Ca^{2+} and NH_4^+ perchlorates at temperatures up to 170°C.[75] Above 300°C the latter decomposes leaving a residue of anhydrous $Ca(ClO_4)_2$.

The heat capacity of $NaClO_4$ in the range 11 to 340K has been measured in a vacuum adiabatic microcalorimeter; Zalukaev et al.[76] reported the thermodynamic functions calculated from these measurements. A study of the reactions of $MClO_4$, M = Rb or Cs, with $Hf(ClO_4)_4$ in $HClO_4$-Cl_2O_7 has shown that perchlorato complexes of Hf are formed, e.g. $Cs_n[Hf(ClO_4)_{4+n}]$, n = 1, 2 or 3.[77] The same products were also formed using $HfCl_4$ and MCl as starting materials. A Raman investigation of KXO_4, X = Cl or Br, in anhydrous HF has shown that partial protonation takes place:[78] perbromic acid was thus detected and was shown to be a significantly stronger acid than $HClO_4$ in this medium. Tetraphenylphosphonium perbromate, prepared from Ph_4PBr and $KBrO_4$, was characterised by its vibrational spectra and was shown to be isostructural with the corresponding perchlorate.[79] Villemin and Ricard[80] have investigated a number of oxidations of organic reagents by periodate supported on either an anion exchange resin or, better still, on alumina.

7.1.5 Hydrogen Halides

Equilibrium geometry parameters, proton affinity and other quantities have been calculated for H_2F^+ in the ground state.[81] The dissociative ionisation of monofluoroacetic acid in the gas phase affords an ion, m/z = 34, CH_3F^+, whose collisional activation mass spectrum differs from that of $CH_3F^{\cdot +}$.[82] Halim et al. attribute the former to $HF{\rightarrow}CH_2^{\cdot +}$, which they describe as a novel, stable ion-dipole complex.

The complexes formed by the reaction of HF and NH_3 when codeposited with argon at 12K have been investigated by i.r. spectroscopy.[83] Both the 1:1 and 2:1 adducts were identified. Andrews et al. have investigated the hydrogen-bonded complexes formed between H(D)F and C_2H_2[84] and methylacetylenes.[85] Similarly studied were the reaction products of the addition of HX, X = Cl, Br or I, to C_2H_2 and $C_2HF(Cl)$ as well as the vacuum UV photolysis products of vinyl halides and dihaloethylenes. The H-bond complexes were inferred to be π bonded although there was some evidence for σ complexes as well in the C_2HF-HF system. Similarly, the interaction of substituted alkenes and HF in Ar matrices showed π-hydrogen bonded complexes;[86] the H-bonding was said to be stronger with the methyl substituted alkenes. However vinyl fluoride-HF was classed as a σ complex. A photoelectron spectroscopic study of the H-bonded species $Me_2O.HF$ and $Me_2S.HF$ has appeared.[87] This provides definitive spectroscopic identification of these adducts.

Redington[88] has reconsidered the evidence for the molecular structures present in the vapour of HF; he offers an analysis of existing data which points to the existence of mainly cyclic, $(HF)_2$-$(HF)_{12}$ species. The alkylation of methane, ethane, propane, and n-butane by ethene has been investigated in homogeneous HF-TaF_5 systems:[89] isomerisation of the hexanes and oligomerisation-cracking processes caused problems. Devynck et al.[90] have shown that n-C_5H_{12} and C_3H_8 are oxidised faster by protonated fluoranil, 2,3,5,6-tetrafluoro-p-benzoquinone, in HF-SbF_5 solutions than by H^+ itself. Reaction rates were measured and also it was shown to be possible to oxidise the dihydrofluoranil electrochemically at a potential below that at which the lighter alkanes are affected. The reaction of titanium metal in anhydrous HF-SbF_5 unexpectedly yields Ti(II) solutions;[91] in solutions of lower acidity other species, probably Ti(III), are formed. Vanadium and Cr behave more simply and form the +2 metal ions.

The crystal structure of the $H_2O(HF)_2$ phase has been determined at $-100^\circ C$ with greater precision.[92] The structure of the H_2O-$(HF)_4$ phase consists of H-bonded, puckered O_2F_4 rings linked by pairs of $(HF)_2$ units into ribbons. The enthalpies of solution of a variety of inorganic salts, including several alkali metal halides and K_2MF_6, M = Mn, Re and Si, have been measured in 0, 12, 24 and 48% w/w aqueous hydrogen fluoride.[93] From these results and appropriate extra thermodynamic assumptions Peacock and coworkers estimated enthalpies of transfer of the constituent ions from water into hydrofluoric acid. Adachi[94] has described the use of hydrofluoric acid-boric acid media in new cation and anion exchange methods for the separation of metals which form stable fluoride complexes e.g. Zr, Ti, Al and U. A series of graphite fluoride intercalation compounds, $C_n^+HF_2^-.2H_2F_2$, are formed electrochemically and reversibly from aqueous solutions over the HF concentration range 5 to 50 mol/l.[95]

The indole-formyl protecting group for tryptophan in solid phase peptide synthesis can be removed efficiently and quantitatively by a new reagent cocktail, HF-Me_2S-p-thiocresol-p-cresol, 25:65:5:5 by volume.[96] Merrifield and his colleagues also reported that this cleavage of benzyl alcohol-derived protecting groups is possible with a 1:3 mixture of HF and Me_2S. The kinetics of the reaction of gaseous HF with $CaCl_2$ have been investigated: the first chloride ion reacts faster than the second.[97]

The differences in the electric dipole moments and polarisabilities of HCl and DCl have been determined;[98] the results are consistent with published spectroscopic data. The solubility of HCl in liquid $SiCl_4$ has been measured by total pressure studies up to 450K and 1.7MPa.[99] Henry's law is obeyed up to x(HCl)=0.02. No specific interaction between the gaseous components was detected. Similar results were obtained for HCl in $GeCl_4$. The e.s.r. spectrum of the product of the reaction of potassium and HCl in an Ar matrix has been assigned to the previously unobserved σ* radical HCl^-.[100]

Several molecular complexes formed between HCl and Me_2O in inert matrices have been studied by i.r. spectroscopy.[101] The spectroscopic properties of the 1:1 complex were analysed in detail in the light of current theories of H-bonding. The H-bonded heterodimer of cyclopropane and HCl has been investigated in the gas phase.[102] The interpretation of the spectroscopic data favours an edge-on adduct of C_{2v} symmetry with the HCl coplanar to the ring and bonded to the mid-point of one C-C bond.

The rotational spectra of the dimers, H_3P-HX, X = Cl or Br, have been detected using the recently developed technique of Fourier transform microwave spectroscopy.[103] The proposed geometry, C_{3v}, is consistent with H-bonding from the halogen to phosphorus. Molecular interaction between HI and Me_2O in N_2 matrices have been studied by i.r. spectroscopy.[104] Three complexes were identified, 1:1 and two 1:2, $(Me_2O)_2H^+I^-$, each having a distinct potential function for the proton.

Elsemongy and coworkers have determined the thermodynamic properties of HCl in water-1,2-dimethoxyethane[105] and HBr in water-acetone[106] and -ethyleneglycol[107] mixed solvent systems.

7.2 HYDROGEN

7.2.1 The Element

Kita and Stedman[108] have reported on the kinetics of the reactions between hydrogen atoms and HCl, Cl_2 and NOCl. The electron-impact ionisation of neutral mixed clusters composed of H_2O-ROH, R = Me or Et, molecules results in the formation of $[(ROH)_n(H_2O)_m]H^+$ ion clusters.[109] Clusters having $n+m < 25$ have been detected in a molecular beam mass spectrometer. Results show that for m = 1 the proton is preferentially solvated by MeOH, for n = 9, and by EtOH, for n = 10. Schwartz et al.[110] have proposed that cp_2ZrRCl, R = alkyl, activate H_2 by the heterolytic reaction (10). Qualitatively the rates for hydrogenation by a series of Zr

$$cp_2ZrRCl + D_2 \rightarrow cp_2ZrDCl + RD \qquad \ldots(10)$$

complexes were:

$$cp_2ZrRH > cp_2ZrRCl \simeq cp_2ZrR_2 > [(cp_2ZrCl)_2(\mu\text{-}OCHR)] > cp_2Zr(COR)Cl.$$

This trend is the same as that for carbonylation and thus suggests a possible link between the two mechanisms.

A report on the enrichment of low concentrations of tritium present in H_2 and D_2 (as HT and DT) describes how this may be achieved by means of thermal diffusion.[111] Studies of the T + H_2 and T + D_2 systems moderated by He, Ar or Kr have been reported.[112] The kinetic parameters indicate that He is a much poorer moderator than the other two gases studied.

The reaction of H_2 with CO over Pd/La_2O_3 gives MeOH with 89% selectivity;[113] acidic catalyst supports, as in Pd/SiO_2, favour the formation of CH_4. A microwave discharge of a mixture of CO_2 + CH_4 produces CO + H_2:[114] the standard enthalpy change for this reaction is +247 kJ mol^{-1}.

A new thermochemical cycle consisting of the sequence of reactions (11)-(14) has been proposed[115] as a possible basis for

$$2MgO(c) + SO_2(aq) + I_2(c) \xrightarrow{70^oC} MgSO_4(aq) + MgI_2(aq) \qquad \ldots(11)$$

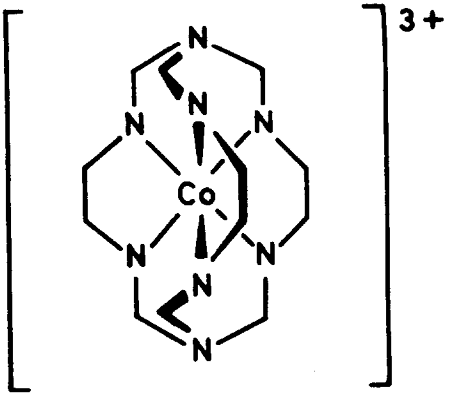
$$MgSO_4(aq) + MgI_2(aq) \xrightarrow{400^oC} MgSO_4(c) + MgO(c) + 2HI(g) + nH_2O(g) \qquad \ldots(12)$$

$$MgSO_4(c) \xrightarrow{1100^oC} MgO(c) + SO_2(g) + (\tfrac{1}{2})O_2(g) \qquad \ldots(13)$$

$$2HI(g) \xrightarrow{300-700^{\circ}C} H_2(g) + I_2(g) \qquad \ldots(14)$$

hydrogen production: Mizuta and Kumagai report fresh experimental data on reactions (11) and (12).

Electrochemical and photochemical studies have shown that $Co(\eta-C_5H_4CO_2H)_2^+$ and $Cosep^{3+}$, (10), function as one electron transfer mediators and H_2 generating relays in aqueous systems.[116]



(10)

7.2.2 Hydrogen-Bonding

Taylor and Kennard[117] have surveyed the structures of compounds showing C-H...X, X = O, N or Cl interactions as determined by neutron diffraction methods; they concluded that these interactions are more likely to be attractive than repulsive. The ^2H n.q.r. spectra of several compounds having non-linear H-bonds, more specifically O-H...O angles less than 150°, have been obtained at 77K for a range of organic compounds.[118] The values observed for the quadrupole coupling constants are higher than those found in a linear H-bond having the same O...O distance.

Larson and McMahon[119] have reported the first completely experimental determination of the H-bond energy in gaseous FHF^-. This was achieved by setting up a relative scale of fluoride ion binding energies for a range of gaseous Brønsted acids, Figure 2: this scale was made absolute by two independent data, namely (i) the F^- affinity of ketene, and (ii) Kebarle's datum for $D(F^--H_2O)$.

The values obtained for D(F^--HF) in this way were 39.1 and 38.6 kcal mol^{-1}. The use of isotopic dilution has allowed an analysis

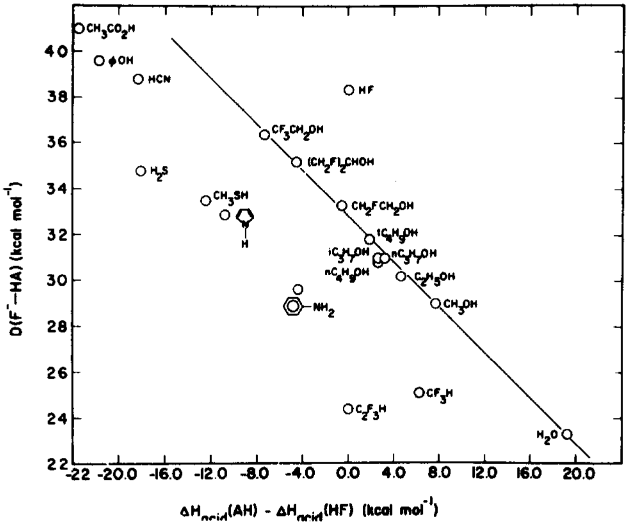


Figure 2. Correlation between fluoride binding energy and gas-phase acidity for a number of gas-phase Brønsted acids of various functional group types. Lewis acids and Brønsted acids with gas-phase acidities that are either unknown or less than that of water were also used to provide successive fluoride transfer equilibria for multiple overlap sequences used to construct the fluoride affinity scale (reproduced by permission from J. Am. Chem. Soc., 104(1982)5848).

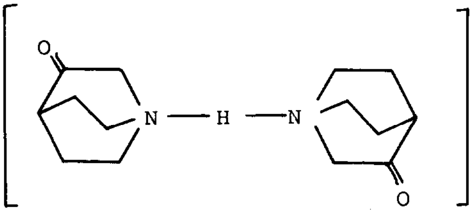
of the i.r. spectrum of HF_2^- in the Me_4N^+ salt.[120] The assigned spectrum indicates that the H-bond is stronger in this salt than in KHF_2; Harmon and Lovelace show how this contradiction may be resolved. The spectrum of the analogous p-toluidinium salt was assigned on the basis of a weak and unsymmetrical H-bond. The i.r. spectra of HF_2^- in several different alkali metal halide single crystals are consistent with a linear symmetrical species when the overall structure is of the NaCl or CsCl type.[121]

Jacobs and co-workers[122] have prepared $CsOH.H_2O$ as a by-product in a CsH synthesis; the monohydrate was recrystallised from NH_3 in high pressure autoclaves (490K). Single crystal X-ray data show a H-bonded layer structure at 355 and 400K for the anions: the O-O intralayer distance is 2.64Å. Infrared spectroscopic and thermochemical data were also presented. Additional transition metal metal cluster compounds containing the $H_3O_2^-$ ligand have been reported.[123] In two of these the anion is symmetric with O-(H)..O separation of 2.51Å.

An i.r. study of a number of phases of composition $R_4NNO_3.nHNO_3$, n = 2, 3 or 6, has appeared.[124] The effect of n on the nature of the H-bonding was discussed. Two new compounds containing the hydrogen dinitrato anion have been characterised by Gillard et al.[125] Trans-$[Rupy_4Cl_2]H(ONO_2)_2$ is isomorphous with the Rh(III) analogue but has additional disorder involving the nitrate groups owing to the facile loss of nitric acid. The other compound described contains the protonated phenanthridine cation. A very short H-bond with O-(H)...O = 2.432(2)Å links the two parts of the $SO_4HSO_4^{3-}$ dimer in the trisodium salt:[126] this bond is asymmetric on the basis of new diffraction data. The largest thermal vibrational of H is practically normal to the bond in contrast to findings in other short O-H...O bonds. This result is compared with other neutron diffraction studies of O-H...O bonds with distances less than 2.50Å.

The structure of potassium hydrogen bis(p-fluorobenzoate) has been shown by X-ray methods to contain a short, apparently symmetrical H-bond with O-H...O distance of 2.460(4)Å.[127] The structure of potassium tetroxalate, $KH_3(C_2O_4)_2.2H_2O$, has been redetermined to give a chemically acceptable structure ($P\bar{1}$ space group).[128] Extinction errors needed to be dealt with and may have influenced a previous re-determination in the P1 space group. The structure of $Na_3AsS_4.8D_2O$ has been refined from neutron and X-ray data:[129] it consists of hexacoordinated Na^+ and AsS_4^{3-} ions linked to form corrugated layers. A variety of H-bonded systems were identified and these results were correlated with single-crystal Raman spectra on the $8D_2O$, $8H_2O$ and isotopically dilute HDO variants. A centrosymmetric short (O-H...O = 2.41(1)Å) H-bond has been observed in $(pyO)_2H^+ AuCl_4^-$, pyO = pyridine N-oxide.[130]

Guanidinium tetraphenylborate, $C(NH_2)_3BPh_4$, reacts with N,N'-ethylenebis(salicylideneaminato)nickel(II), Ni(salen), in THF to form the 2THF solvate of the 1:3 adduct.[131] The structure of the product shows that the guanidinium ion is (i) encapsulated in a cage of six oxygens of the three Ni(salen) units, and (ii) is held in place by six strong H-bonds. Similar reasons are thought to be responsible for complexation of alkylammonium salts with complexes similar to Ni(salen). Neutron diffraction studies have provided evidence for the existence of the hydrogen diquinuclidinone homoconjugated cation (11).[132] The N-(H)...N



(11)

distance, 2.635(2)Å, is clearly very short and bond was reported to be linear and symmetrical.

A number of F-H...O bonded systems have been described by Emsley, Clark and coworkers[24-27] and are mentioned briefly in Section 7.1.2. Equilibrium constants for reactions typified by equation (15) have been measured for 40 gas phase systems by means

$$RH + Cl^- \rightarrow RHCl^- \qquad ...(15)$$

of high pressure mass spectrometry under chemical ionisation conditions.[133] For RH = oxygen acids the binding free energies increase with the gas phase acidity of RH; this generalisation does not hold for the carbon acids studied.

An alternative synthesis of $Ph_4As[HCl_2]$, its crystallography and vibrational properties have been reported.[134] The H-bonded anion is situated on an inversion centre with Cl--(H)--Cl = 3.09Å. The i.r. and Raman spectra confirm the symmetrical nature of the anion. Quantum chemical and statistical thermodynamic methods have been applied to the interaction of CHX_3, X = Cl or F, with the formamide dimer.[135] The results indicate that chloroform, but not fluoroform, is capable of perturbing the N-H...O=C model system on account of the formation of a formamide-chloroform H-bonded dimer.

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