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Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 THE HALOGENS

7.1.1 The Elements

Rate constants have been measured for the homogeneous recombination of F atoms, with F_2, He, or Ar as third bodies:[1] they show that F_2 is approximately 60% more efficient as the third body than either He or Ar. Fluorine reacts with water to produce H_2O_2.[2] The results of the kinetic study are consistent with a mechanism involving the following steps, equations (1) to (4).

$$F_2 + H_2O \xrightarrow{k_1} HOF + HF \quad ...(1)$$

$$HOF + H_2O \xrightarrow{k_2} H_2O_2 + HF \quad ...(2)$$

$$F_2 + H_2O_2 \xrightarrow{k_3} O_2 + 2HF \quad ...(3)$$

$$HOF + H_2O_2 \xrightarrow{k_4} O_2 + HF + H_2O \quad ...(4)$$

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At 1°C the value of k_1 was given as $10^{5.0(\pm 0.3)} s^{-1}$. The use of the term "positive fluorine" continues to be discussed.[3]

Barnette[4] has reported that N-fluoro-N-alkylsulphonamides are effective reagents for selective fluorination of a broad variety of carbanions under mild conditions. These fluorinated sulphonamides are readily prepared by reaction (5) and are, in general, stable compounds. Shreeve and Gupta[5] have described a

$$RSO_2NHR' + F_2 \xrightarrow[-78°C]{N_2} RSO_2NFR' + HF \qquad ...(5)$$

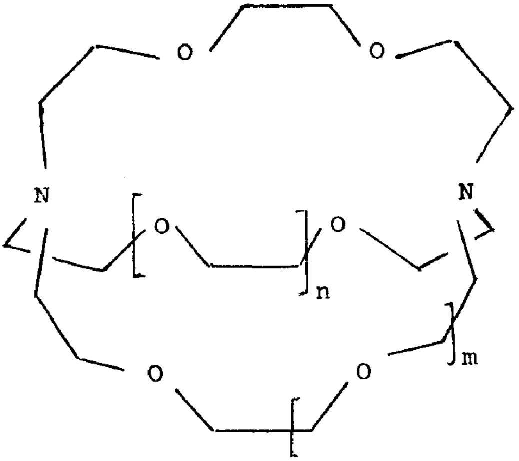
series of fluorination reactions of COF_2 in which either oxidative addition at the central atom (P or N but not As, reaction (6)) occurs or H-displacement from P-H, N-H, or C-H bonds, reaction (7), takes place.

$$Ph_2PCH_2CH_2AsPh_2 + COF_2 \xrightarrow{25°C} Ph_2PF_2CH_2CH_2AsPh_2 + CO \qquad ...(6)$$

$$Me_2NH + COF_2 + Et_3N \rightarrow Me_2NF + Et_3NHF + CO \qquad ...(7)$$

Radiofluorination of potassium arylpentafluorosilicates, $K_2[ArSiF_5]$, with ^{18}F-labelled acetylhypofluorite in acetic acid, gives ^{18}F-labelled ArF in 6-20% yield.[6] Similar yields were obtained by Diksic et al[7] by the direct fluorination of arylsilanes. The use of F_2 and $MeCO_2F$ in generating labelled ArF have been compared[8] when aryltin derivatives are employed as the source of aryl groups. The yields of labelled products were consistently high (ca. 70%) from the acetylhypofluorite reaction and much more variable (54 to 95%) from the F_2 reaction. Visser and coworkers[9] recommend the hypofluorite as fluorinating agent for cleaving arylmercury compounds.

Molecular Br_2 or I_2 interact with [2.2.2], [2.2.1] and [2.1.1] cryptands in $CHCl_3$ to form 1:1 complexes. The authors present evidence to show that these complexes may be regarded as "positive halogen" cryptates;[10] thus they are destroyed by protonic acids or alkali metal salts, moreover ICl and Ipy_2NO_3 produce complexes with identical ^1H n.m.r. spectra to that from the I_2-cryptand. DesMarteau et al[11,12] have reported the caesium fluoride-promoted bromination of $CF_2{=}NX$, X = Cl or Br, see Section 5.1.7, in which



[2.2.2] m = n = 1

[2.2.1] m = 1, n = 0

[2.1.1] m = n = 0

the active species is believed to be $CsF.Br_2$. New systems using I_2 and nitriles, such as MeCN or polyacrylonitrile, as anodic substances have been shown to be effective for storage of electrical energy.[13] Equation (8) was proposed to account for the anodic storage process with $LiBF_4$ as the supporting electrolyte in MeCN. The crystal structures of four neutral charge-transfer

$$\tfrac{1}{2}I_2 + MeCN \xrightarrow{-e} (MeCN.I)^+ \qquad \ldots(8)$$

molecular compounds formed between dithizone or ethylenethiourea, as donors, and I_2, as acceptor, have been reported.[14]

7.1.2 Halides

"Fluoride, The Aging Factor" by Yiamouyiannis,[15] discusses aspects of the toxicity of fluoride and concludes that there is no safe level for fluoride in food or drinking water. Analysis, by statistical pattern recognition, of the results of Monte Carlo simulations for F^- and Cl^- in aqueous solution offers[16] a distorted square pyramidal structure for $F(H_2O)_5^-$ and a distorted tricapped trigonal prism for $Cl(H_2O)_9^-$. Burdett et al[17] have discussed the effect of the presence of highly electronegative ligands, fluorine and the noble gases, on the bond lengths and site preferences of ligands in small molecules. They presented a coherent and versatile scheme that is able to rationalise the unusually short and long distances found in XAB systems, where X = noble gas, halogen or hydrogen, and A,B = halogen, carbon, nitrogen, oxygen or sulphur.

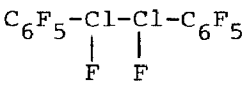
The influence of the source of F^-, in a series of alkylations of phenols catalysed by fluoride, has been studied by Alauddin and Miller.[18] Both C- and O-alkylations were reported depending on the combination of salt and medium used. An ^{18}F tracer study of the interaction of HF with chlorofluoroethanes over a commercial chromia catalyst at 623K has indicated that a surface fluoride is involved:[19] evidence was presented for the formation of three different fluoride species.

Hefter[20] has measured the concentration of free fluoride ion in aqueous perchloric acid electrochemically. His data show that there is no evidence for the presence of H_2F^+ for $[H^+]/[F^-]$ ratios up to 5×10^4. The complexation of alkali metal ions by fluoride was similarly investigated:[21] stability constants were determined for LiF, NaF, and KF at 25°C (1M ionic strength) and also, over a range of temperature, for LiF and NaF. Perachon and coworkers have determined ΔH°_f for $NH_4HF_2(c)$, -809.9 ± 0.9 kJ mol^{-1}, from the measured enthalpies of solution of NH_4F and NH_4HF_2 in aqueous HF.[22] They have also continued with a study of the electrical conductivity of hydrofluoric acid solutions of fluorides (NH_4F, NaF).[23]

A new method of producing chloride ion adducts, $A.Cl^-$, via a series of bimolecular ion-molecule reactions involving chloroformate esters has been described by Larson and McMahon:[24] A may be either a Lewis acid or a Brønsted acid. In this way the relative Cl^- ion affinities of 20 compounds have now been measured; the results were found to be in good agreement with values obtained by other methods. The Cl^- ion binding energies of a range of protic substrates were obtained in this way and were shown to be consistent with far more electrostatic character in the bond than those for fluoride ion.[25]

7.1.3 Interhalogens and Related Species

Obaleye and Sams[26] have claimed to have isolated the substituted dichlorane (1) from the reaction of C_6F_5Cl with F_2.



$$C_6F_5-\underset{\displaystyle F}{\underset{|}{Cl}}-\underset{\displaystyle F}{\underset{|}{Cl}}-C_6F_5$$

(1)

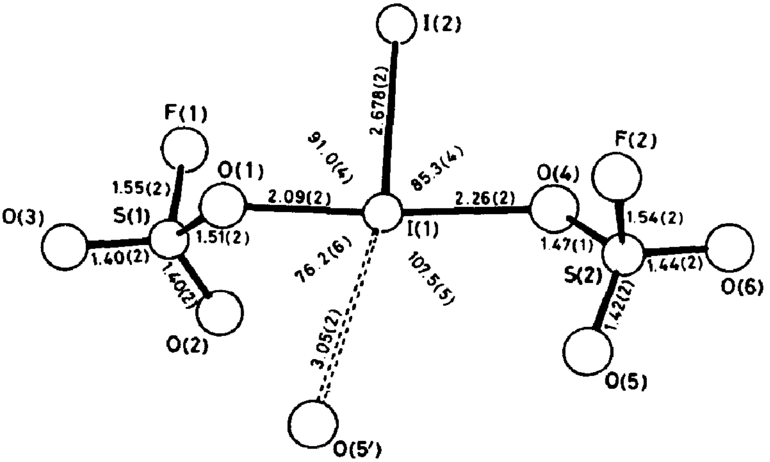
The product, a colourless liquid, was inadequately characterised considering that it represents a new class of compound. Although ClF_5 can be oxidised by either KrF^+ or PtF_6 to $ClF_6{}^+$, the analogous fluorination of BrF_5 can be effected by KrF^+ and not by PtF_6.[27]

The products of the liquid phase fluorination of C_6H_6 with ClF_5 have been investigated:[28] substitutive fluorination was found to be more favoured in this system than in the reactions of the other chlorine fluorides, BrF_3, or IF_5. The reaction between BrF_3 and $C_6F_5SiF_3$ in CCl_3F, equation (9), produces $C_6F_5BrF_2$ as a colourless solid, m.p. 35-36°C, with different properties[29] from

$$BrF_3 + C_6F_5SiF_3 \xrightarrow{0°C} C_6F_5BrF_2 + SiF_4 \qquad \ldots(9)$$

those described by Obaleye and Sams in 1981. The new compound could be converted to the bis(trifluoroacetate) by reaction with $(CF_3CO)_2O$.

Gillespie and coworkers[30] have reinvestigated the product of the reaction between I_2 and $S_2O_6F_2$ in 1:1 proportions. The structure of the product in the solid state has now been determined by X-ray methods, Figure 1; the product is clearly iodine(III) bis-fluorosulphate iodide, $I(SO_3F)_2I$, and not iodine(I) fluorosulphate. The product is, however, remarkable for the bonding I-I distance (2.68Å) which is marginally longer than that in I_2(gas), 2.66Å.



<u>Figure 1.</u> The $I(OSO_2F)_2I$ molecule, showing bond distances (Å) and angles (°).

Substitution reactions of IF_5 with trimethylsilyl-protected bifunctional alcoholates has led to the isolation of mononuclear chelates containing the $I[O(CH_2)_nO]$, n<4, group or bridged systems when n>4.[31] More highly substituted products such as $IF[O(CH_2)_nO]_2$, n = 2 or 3, and $IF_2(OCH_2)_3CCH_3$ were also characterised. Attempts to prepare $IF_{5-n}(OMe)_n$, with n>1, from IF_5 and $Si(OMe)_4$, have not been successful in that the products lose Me_2O in solution at temperatures as low as 0°C.[32] A typical decomposition process is shown in equation (10): this iodine(V) product was isolated but on standing was converted to

$$IF_2(OMe)_3 \rightarrow IF_2O(OMe) + Me_2O \qquad \ldots(10)$$

an insoluble derivative. There was also evidence that $IF_3(OMe)_2$ undergoes the dismutation reaction (11). The ultimate, isolable

$$2IF_3(OMe)_2 \rightarrow IF_4(OMe) + IF_2(OMe)_3 \qquad \ldots(11)$$

product of replacing F by OMe was polymeric $IO_2(OMe)$. The observation that IF_7 is a better fluoride ion donor than ReF_7, reaction (12), has been rationalised by lattice energy calculations and thermochemical analysis.[33]

$$IF_7(g) + ReF_6^+AuF_6^-(c) \rightarrow IF_6^+AuF_6^-(c) + ReF_7(g) \qquad \ldots(12)$$

Iodine(1+) exists in the form of ICl in acidic ($AlCl_3$-N-1-butylpyridinium chloride) ionic liquids and as ICl_2^- in the analogous basic media:[34] however I_3^- is stable in the neutral medium whereas in more basic systems I_2Cl^-, I_3^-, ICl_2^- and I^- are produced.

7.1.4 Oxides, Oxide Halides, and Oxoanions

The reaction of HOF with H_2O produces H_2O_2 and O_2, reactions (1) to (4).[2] Since a substantial amount of the O_2, formed according to reaction (4), is directly derived from HOF Appelman and Thompson have postulated an oxygen-transfer mechanism. An examination of the thermochemistry of fluoroxy (ROF) compounds has revealed a striking linear correlation, equation (13), between the bond energy, D, of the O-F bond and the ^{19}F n.m.r. shift, ϕ, relative to $CFCl_3$.[35] The authors interpret this in terms of a

$$D = 48.8 + 0.126(\phi + 140) \qquad \ldots(13)$$

relationship between the paramagnetic shielding of F and the antibonding character of the 3-centre MO formed by R with the π^* orbital of OF.

Aryl fluorides are formed in high yield by the cleavage of aryl-tin or -mercury derivatives with CF_3OF.[36] A gas-solid microchemical method for the synthesis of acetyl hypofluorite has been described.[37] An improved synthesis of $TeF_5(OF)$ has been reported by Schack and Christe,[38] based on equation (14), with yields as high as 95%. Both $TeF_5(OF)$ and $TeF_5(OCl)$ react with fluoroolefins to form F_5TeO-containing fluorocarbons.[39] Perfluorotertiarybutylhypochlorite, ZCl, converts $VOCl_3$, $TiCl_4$, and CrO_2Cl_2 quantitatively into the stable compounds VOZ_3, TiZ_4, and CrO_2Z_2, respectively, with the formation of Cl_2.[40]

$$B(OTeF_5)_3 + 3F_2 \xrightarrow{100°C} 3TeF_5(OF) + BF_3 \qquad \ldots(14)$$

Stabilisation is reported of the chloroperoxy radical, ClOO, produced by photoisomerising ClO_2 sorbed in the aluminosilicate host matrix of cancrinite at 77K.[41] The isotropic e.p.r. spectrum could also be observed and the electronic ground state was assigned to be $^2A''$. The initial reaction between chlorate(III) and MnO_4^- in acid solution at 25°C proceeds according to equation (15):[42] from the pH dependence of the reaction rate a new, lower value for the dissociation constant of $HClO_2$, $(2.70 \pm 0.45) \times 10^{-3}$M, was inferred. The rate limiting steps in the redox processes were said to be better described by an inner-sphere mechanism. The self-exchange rate for the ClO_2/ClO_2^- couple has been calculated to be $1.6 \times 10^2 M^{-1} s^{-1}$.[43]

$$MnO_4^- + 5ClO_2^- + 8H^+ \rightarrow Mn^{2+} + 5ClO_2 + 4H_2O \qquad \ldots(15)$$

The crystal structure of the new compound $ClO_2^+GeF_5^-$ at −105°C has been determined by X-ray methods.[44] The anion consists of GeF_6 octahedra sharing cis vertices: the cations show strong interactions through fluorines situated over the faces of the triangle defined by the ClO_2 unit. The i.r. and Raman spectra of the salt were assigned. The structural features of the analogous

BF_4^- salt were also reported.[45] Lattice energy calculations were carried out on these salts in order to make estimates of the F^- ion affinities of BF_3 and GeF_4.

The reaction of $ClF_2O^+SbF_6^-$ with Cs_2NiF_6 in anhydrous liquid HF has been used to prepare a sample containing 93% $(ClF_2O)_2NiF_6$:[46] the new compound was characterised by vibrational spectroscopy. Thermal decomposition of the complex in vacuo at 110°C produced ClF_3O quantitatively as well as brown NiF_{2+x}. There was no evidence for the formation of unknown ClF_5O. An attempt to produce $ClF_6^+ClO_4^-$ by reaction (16) yielded rather $FOClO_3$ and ClF_5, according to reaction (17), in good yield.[47] The reaction of

$$ClF_6AsF_6 + CsClO_4 \xrightarrow[-45°C]{HF} CsAsF_6 + [ClF_6ClO_4] \qquad ...(16)$$

$$[ClF_6ClO_4] \longrightarrow ClF_5 + FOClO_3 \qquad ...(17)$$

$$CsClF_4O + FOSO_2F \longrightarrow CsClF_4 + SO_2F_2 + O_2 \qquad ...(18)$$

fluorine fluorosulphate with $CsClF_4O$ proceeds according to equation (18) with $FOSO_2F$ behaving as a deoxygenating agent. I.r. spectroscopy of matrix-isolated alkali metal perchlorates has yielded proof of a bidentate interaction of ClO_4^- with the cations Rb^+ and Cs^+.[48] Raman spectra of aqueous solutions of $HClO_4$ have been examined by Ratcliffe and Irish[49] over a wide concentration range and, for two specific concentrations, as a function of temperature. The most significant results were that the apparent symmetry of ClO_4^- decreases at high concentrations and that a new species appear which was described as $ClO_4^-(H^+aq)^+$.

Physical and chemical evidence indicates that solutions of "tert-butyl hypoiodite" in CCl_4, as prepared by reaction (19), is different from the material generated by reactions (20) and (21).[50]

$$3{}^tBuOCl + I_2 \rightarrow \frac{1}{m}[({}^tBuO)_2ICl]_m + \frac{1}{n}[{}^tBuOICl_2]_n \qquad ...(19)$$

$$3{}^tBuOCl + 3AgI \rightarrow ({}^tBuO)_3I + 3AgCl + I_2 \qquad ...(20)$$

$$3{}^tBuOCl + 2I_2 \rightarrow 3KI + ({}^tBuO)_3I \qquad ...(21)$$

Simple salts, e.g. nitrates or triflates, of Cu, Fe, Mn, and Co have been shown to catalyse the oxidation of alkenes or certain hydrocarbons, e.g. cumene, by iodosyl benzene in MeCN.[51] Iodine-127 Mössbauer spectra have been obtained on several phenyl substituted iodine(III) compounds at 4.2K.[52] Coordination of PhIO to Mn porphyrins does not modify the iodine Mössbauer parameters sufficiently to cause confusion with iodine(I) or (V) compounds. Crystals of $PhI(O_2CCF_3)_2$ have been investigated by X-ray methods:[53] coordination of the iodine atom is essentially T-shaped but two secondary bonds of the bridging carboxylates, see Figure 2, involving O(12) and the centrosymmetrically related atom, complete a pentagonal planar arrangement with the three primary ligand atoms to O(21), C(1) and O(11).

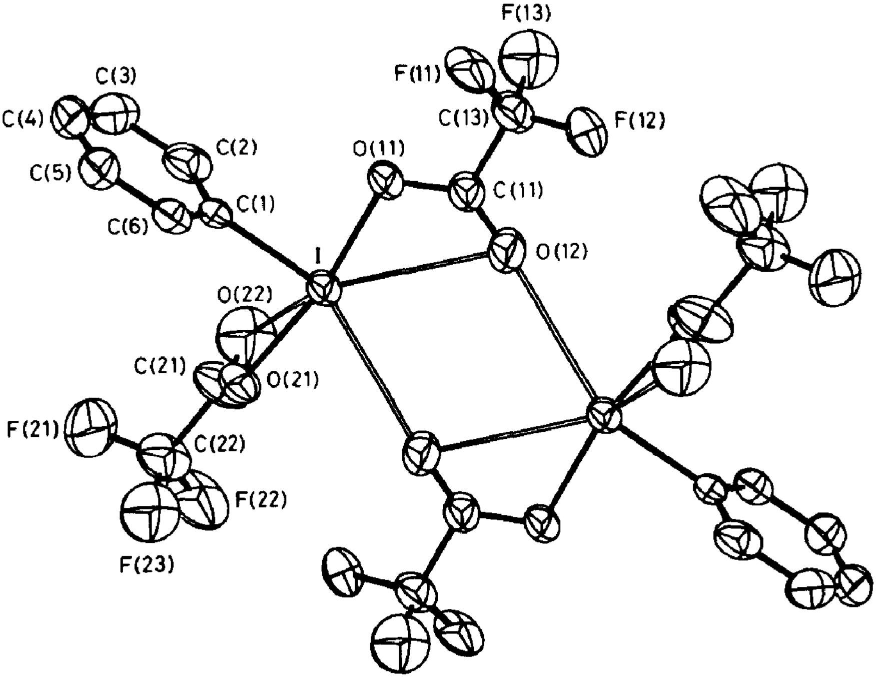


Figure 2. Centrosymmetric dimer of $PhI(O_2CCF_3)_2$, showing the atomic numbering. Only the main fluorine positions are included. Primary bonds are solid, secondary bonds open.

Co-deposition of O_3 and ICl in an inert matrix leads to the formation of the 1:1 complex O_3.ICl, which readily photodissociates ($470 < \lambda < 750$nm) to iodosyl chloride, OICl.[54] A further decomposition product, iodyl chloride, O_2ICl, was thought to be formed by the decomposition of OICl to yield oxygen atoms. From its vibrational spectrum the OIO bond angle was estimated to be 120±10° in O_2ICl. Ferranti and Indelli[55] have confirmed the H^+ ion-dependent pathway for the IO_4^--I^- reaction.

7.1.5 Hydrogen Halides

O'Donnell[56] has offered an explanation for the rapid increase in acidity in progressing from dilute aqueous solutions of HF to more concentrated (ca. 10M) solutions. He also drew attention to the evidence concerning the high Hammett acidity of anhydrous liquid HF, -15.05, and to the lack of buffering action from self-ionisation, as compared with HSO_3F or H_2SO_4. Further examples of the use of polymer-supported HF in organic syntheses have been reported by Gregorcic and Zupan.[57] Ab initio molecular electronic structure theory has been used to predict the structures and harmonic vibrational frequencies of $(HF)_2$ and $(HF)_3$:[58] good agreement was found with recentexperimental data for the dimer.

The formation of $(HF)_n$ in solid Ar has been investigated by FT i.r. spectroscopy.[59] It was shown that the controlled diffusion of HF in the matrix provides a mechanism for the stepwise association of HF giving all multimers in the $n = 2$ to 6 range. It was concluded that oligomers with $n>6$ are not formed under these conditions, 20 to 28K, and therefore it is improbable that higher oligomers will be stable in the gas phase, at higher temperatures. Andrews[60] has published a short review of HF-base complexes studied by FT i.r. spectroscopy: he and Johnson have recently investigated the 1:1 adducts of HF with Me_2CO, MeCHO, and HCHO in Ar matrixes.[61]

Sundermeyer and Klockner[62] have described a process for converting waste HCl to H_2 and Cl_2: the method depends (i) on H_2 formation in a molten salt containing a reactive metal, and (ii) electrolysis of the melt to regenerate the metal and liberate Cl_2.

7.2 HYDROGEN

7.2.1 Protonic Acids

Kebarle et al[63] have investigated the gas-phase basicities of several glymes and crown ethers by measuring proton-transfer equilibria in a pulsed-beam, high ion-source pressure mass spectrometer. They provide a correlation of the basicity of the polyethers with their conformation and chemical structure. The proton affinities of N_2O, CO_2, CH_2N_2, HNCO, CH_2CO, HN_3, MeNC and MeCN have been estimated with an accuracy of ±7 kcal mol^{-1}.[64] Novel, non-oxidising protonic acids, (2), (3), and (4), have found value for protonating transition metal hydrides, e.g. $(Ph_3P)_4CoH \xrightarrow{H^+} (Ph_3P)_4CoH_2^+$. All three acids are crystalline

$(CF_3SO_2)_2CH_2$ (2)

$(CF_3SO_2)_2CHPh$ (3)

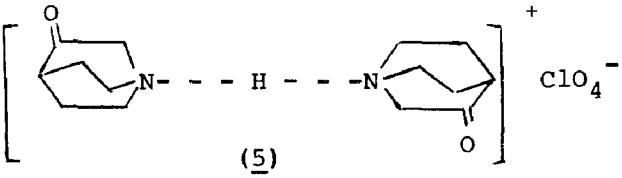
$(CF_3SO_2)_2NH$ (4)

and volatile; (2) and (3) are non-hygroscopic.[65]

7.2.2 Hydrogen-Bonding

The vibrational spectra of $BaF(HF_2)$ at 300 and 90K have been analysed and are shown to be consistent with an unsymmetrical HF_2^- in which the H-F distances are 1.08 and 1.20Å.[66] The crystalline KF-succinic acid adduct contains strong O-H---F^- bonds:[67] the earlier crystallographic evidence has been used to help interpret the vibrational spectra of the adduct.

The effect of temperatures on the N-H---N bond in bis(quinuclidin-3-one)hydrogen perchlorate, (5), has been investigated by X-ray diffraction.[68] The N---N distance decreases with decreasing temperature and the H-bond becomes more symmetrical.



(5)

The crystal structure of tris-2,2'-bipyridinium nitrate hexanitratothorate(IV), $[(bpyH)_3NO_3][Th(NO_3)_6]$, contains the expected ThO_{12}, irregular icosahedral, environment as well as the unusual cation complex.[69] The latter has approximately C_3 symmetry with the three bipyridinium(+1) ions having syn configurations and each being H-bonded to a different oxygen atom of the nitrate ion.

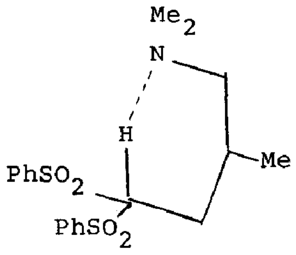
Hydrogen-bond energies in gaseous FHF^-, $XHCl^-$, and $XHCN^-$, where

X = F or Cl, have been determined from ion cyclotron resonance halide-exchange equilibria measurements.[70] The authors predict H-bond energies for similar species based on a linear correlation between shift in frequency in H-bond motion, relative to free HX, and observed bond energies. The crystal structure of 1-methyl-1,3,5,7-tetraazaadamantan-1-ium bromide monohydrate contains a coplanar O_2Br_2 unit associated with $(H_2O.Br^-)_2$.[71] The surprising feature here is that the water molecules form H-bonds to the soft Br^- ions rather than to the hard tertiary amino atoms of the $[(CH_2)_6N_4Me]^+$ cation. The macrocyclic polyether 18-crown-6 forms crystalline 1:1 complexes with $BF_3.NH_3$ and $BH_3.NH_3$.[72] The structures of these complexes show H-bonding of the NH_3 units with three crown ether oxygens.

The structure of $Na_2S.5H_2O$ differs from that of the nonahydrate in containing no O-H---O interactions, only O-H---S bonds.[73] These were characterised by X-ray and vibrational spectroscopic methods: the O---S distances were shown to be 3.30, 3.32, and 3.45Å. The crystal structure of $N_2H_6(BF_4)_2$ has been determined by X-rays:[74] the $N_2H_6^{2+}$ and BF_4^- ions are apparently linked by a network of non-linear H-bonds with N---F distances ranging from 2.68 to 3.03Å. A survey of 1509 N-H---O=C hydrogen-bonds, investigated by diffraction methods in 889 organic crystal structures has shown that about one fifth are bifurcated and only six are trifurcated:[75] the remainder are two-centred and essentially linear.

The high proton affinity and negative entropy of protonation of $MeCONHCH(Me)CO_2Me$ as compared with DMF are consistent with intramolecular H-bonding in protonated N-acetylalanine.[76] Pulsed high-pressure mass spectrometry of hydrogen-bonded $N-H^+---O$, $N-H^+---N$, and $O-H^+---O$ systems has reinforced the linear correlation between bond dissociation energy and the difference in proton affinities.[77]

The X-ray structure determinations of three adducts of 1,8-biphenylenediol with O-donors, HMPA, 1,2,6-trimethyl-4-pyridone, and 2,6-dimethyl-γ-pyrone, show clearly that two short (O-H---O distance ca. 2.6Å) H-bonds are formed to the same oxygen in each adduct.[78] Harlow and coworkers[79] have identified a short C-H---N interaction in 4,4-bisphenylsulphonyl-2,N,N-trimethylbutylamine, (6), by X-ray crystallography. The H---N distance is 2.34Å and the C-H---N angle 138°. N.m.r. studies on the compound, as well as of some related compounds, in CD_2Cl_2 are consistent with C-H---N bonding persisting in solution.



(6)

7.2.3 Hydrogen as a Ligand

Irridation with u.v./visible light of surface-active $(bpy)_3Ru^{2+}$, deposited as a monolayer on glass, in contact with water, produces H_2:[80] the Ru complex was shown to migrate to other sites where it continues to function as an active catalyst. The replacement of 10 to 20% Ni by Al in the alloy $CeNi_5$ produces a material with excellent H_2-storage properties.[81] Hydrogen densities of such materials, relative to liquid H_2, are in the range 1.1 to 1.3. The vapour pressure of the hydrides of $CeNi_{5-x}Al_x$ at room temperature can be expressed as $p_{H_2}(atm) = 1365.8e^{-9.55x}$: H_2 sorption rates are extremely rapid, 60 to 200s for completion.

The first transition metal complexes containing coordinated dihydrogen have been isolated and characterised.[82] Toluene solutions of $M(CO)_3(Pcy_3)_2$, M = Mo or W, cy = $c\text{-}C_6H_{11}$, react with H_2 at 1 atm. at ambient temperature to form yellow, crystalline, mer,trans-$M(CO)_3(Pcy_3)_2(H_2)$ in high yields. The structure of $W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)$ was established by X-ray (-100°C) and neutron diffraction studies. The dimensions of the novel ligand were established; the H-H distance is 0.75(16)Å (X-ray) or 0.84Å (neutron) as compared with 0.74Å in the free molecule. The vibrational spectrum was assigned with ν(H-H) at $2690cm^{-1}$ for $W(CO)_3(Pcy_3)_2(H_2)$: the ^1H n.m.r. spectrum of $W(CO)_3(P^iPr_3)_2(HD)$ contained a resonance at 14.2τ showing a 33.5Hz coupling to deuterium.

An unusual hydrido complex of rhenium has been prepared by the reaction of $(Et_4N)_2ReH_9$ and $MeC(CH_2PPh_2)_3$ in MeCN:[83] X-ray studies demonstrated that the product $Et_4N[Re_2H_7(MeC(CH_2PPh_3)_3)]$.MeCN contains the $Re_2(\mu\text{-}H)_3$ group and that one of these Re atoms has four terminal hydride ligands, such that the coordination of that Re approximates to a pentagonal bipyramid of hydrogens.

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