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Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 THE HALOGENS

7.1.1 The Elements

The reaction of aryltrimethylammonium perchlorates with ^{18}F-labelled fluoride in DMSO yields the "no carrier added", ^{18}F-labelled aryl fluoride in high yield, equation (1), even under mild conditions.[1] Regioselective incorporation of radiofluorine into simple aromatic molecules can be accomplished by fluorinating aryltrimethylsilanes under mild conditions with ^{18}F-labelled reagents such as $[^{18}F]F_2$ or $CH_3CO_2{}^{18}F$, generated in situ.[2] Although complicated by ring fluorination processes the synthesis of labelled aryl fluorides in these ways appears superior to most other methods.

$$PhNMe_3{}^+ + ClO_4{}^- + M^+F^- \rightarrow PhF + M^+ + ClO_4{}^- + NMe_3 \qquad \ldots(1)$$

Core-ionisation and Auger kinetic energies for the halogens, as well as for the hydrogen halides and ClF, have been analysed, see Table 1, to give the relative electrostatic potential at the

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Table 1. Comparison of Experimental and Theoretical Core-Ionisation (ΔI), Ground-state Potential (ΔV) and Relaxation (ΔR) Energies (eV) for HX and ClF relative to X_2.

molecule	ΔI(exptl)	ΔI(calcd)	ΔV(exptl)	ΔV(calcd)	ΔR(exptl)	ΔR(calcd)
F_2	0.0	0.0	0.0	0.0	0.0	0.0
HF	-2.40(9)	-2.11	-5.36(15)	-4.48	-2.96(7)	-2.37
ClF	-2.11(7)	-2.04		-1.79		0.27
Cl_2	0.0	0.0	0.0	0.0	0.0	0.0
HCl	-0.44(6)	-0.56	-1.53(10)	-1.54	-1.09(5)	-0.98
ClF	1.36(6)	1.43	0.54(10)	0.62	-0.82(5)	-0.81
Br_2	0.00	0.00	0.00	0.00	0.00	0.00
HBr	-0.04(7)	-0.07	-0.94(15)	-1.13	-0.90(11)	-1.06
I_2	0.00	0.00	0.00	0.00	0.00	0.00
HI	0.27(6)	0.18	-0.75(10)	-0.68	-1.02(5)	-0.85
I	1.0(2)		-0.1(3)		-1.1(1)	

halogen atom and the relaxation energy that arises from valence rearrangement upon core ionisation.[3] Using a point-charge model the initial-state potentials were derived; these are consistent with chemical experience.

$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3 \qquad ...(2)$$

Reaction (2) has been studied by FTIR spectroscopy and by a static wall-less u.v. absorption technique.[4] An upper limit to the homogeneous bimolecular rate constant of 10^{-19} cm^3 $molecule^{-1}$ s^{-1} was established, signifying that this reaction is unimportant in the stratosphere. It has been reported that a product of the photo-oxidative degradation of organochlorine compounds in the atmosphere is trichloromethylhydroperoxide, Cl_3COOH.[5] It is formed in sunlight from chloroform and O_2 and is unexpectedly stable; it reacts with N_2O_5 to give Cl_3COONO_2 and with acetyl chloride to give $Cl_3COOCOMe$. In the course of a study of the oxidation of aqueous $Pt(CN)_4^{2-}$ by Cl_2 and HOCl, Drougge and Elding[6] have redetermined the kinetics of hydrolysis of Cl_2, equation (3); $k_3 = 8.7 \pm 0.2 s^{-1}$ and $k_{-3} = (2.66 \pm 0.03) \times 10^4 M^{-2} s^{-1}$ at 25°C in 1M perchlorate medium.

$$Cl_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HOCl + H^+ + Cl^- \qquad ...(3)$$

Cady[7] has redetermined the composition of bromine hydrate, $Br_2.nH_2O$, formed when the gaseous reagents are condensed on to a surface at ca. 0°C. The values of n ranged from 7.8 to 8.6; values greater than 9 were attributed to samples containing unreacted water. Fuchs and coworkers[8] have described the use of certain substituted anthraquinone (AQ) derivatives as catalysts in the photolytic oxidation of HBr to Br_2. A continuous O_2-flow was used to help transfer the Br_2, up to 0.3mmol h^{-1}, equation (4), from the photolytic cell.

$$2HBr + \tfrac{1}{2}O_2 \xrightarrow{h\nu/AQ} Br_2 + H_2O \qquad ...(4)$$

The method for determining radioiodine in cow's milk has been improved.[9] Iodine can be made from iodide in the reaction with hydrogen peroxide using $FeSO_4$ as the catalyst.[10] The presence of high concentrations of Cl^- or Br^- in either natural or synthetic brines has no effect on the reaction specificity or kinetics. This approach offers a potentially less caustic method for the recovery of iodine from brine as compared with the most commonly used Cl_2-displacement processes. A subiodide of tellurium, previously formulated as Te_3I, has been re-investigated.[11] The composition apparently can range from Te_2I to $Te_2I_{0.42}$; the structure of the iodine-richest phase, Figure 1, consists of planar double layers of Te_2 units (Te-Te, 2.713(7)Å) alternating with layers of I_2 molecules (I-I, 2.866(12)Å) having longer, 3.324 and 3.841(16)Å, intermolecular contacts. The shortest interlayer distance, I--Te, is 3.812(9)Å. This phase can be described as a tellurium intercalate and, in the crystal studied, the occupation of the iodine layer was only 88 percent. Thermal decomposition of the phase begins at ca. 100°C with the loss of I_2 and the growth of Te crystals: eventually TeI_2 vapour is lost.

Iodine addition to perfluoroalkyl alkynes, $R_fC{\equiv}CH$, affords the corresponding diiodoalkenes.[12]

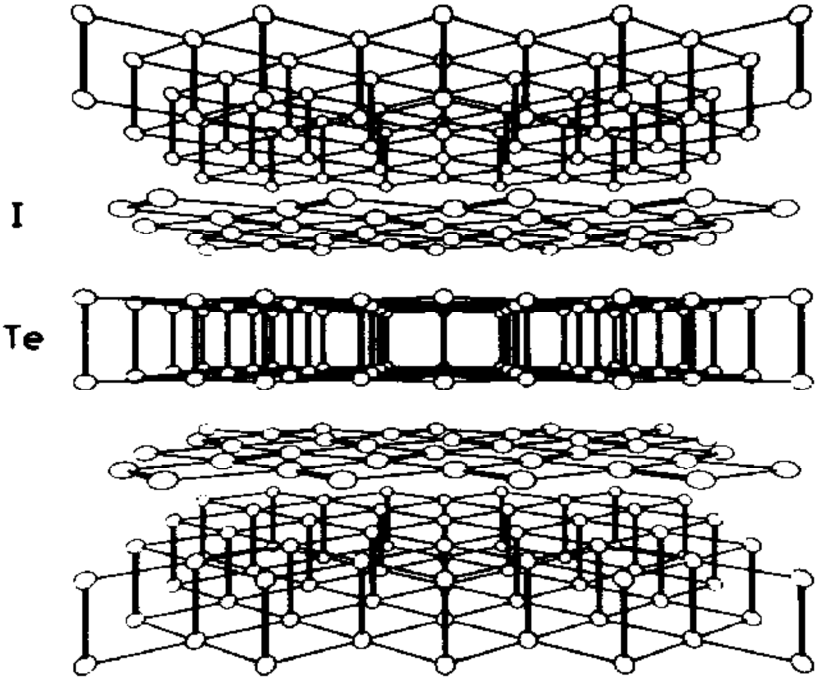
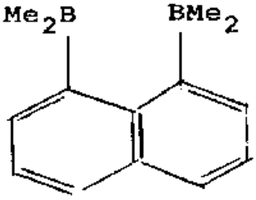


Figure 1. Perspective view of the layer sequence [001] in Te_2I. Te_2 pairs and I_2 molecules are represented by bolder lines (reproduced by permission from Angew. Chem., Int. Ed. Engl., 24(1985)393).

7.1.2 Halides

The behaviour of 1,8-naphthalenediylbis(dimethylborane) (1) towards the anhydrous F^- ion yields an anion whose ^1H and ^{19}F n.m.r. data indicate a fluoride-bridged structure.[13] By contrast (1) appears to interact but weakly with Cl^- and Br^- ions. Hudlicky[14] has reported ^{19}F n.m.r. shifts of HF, some ionic fluorides and hydrogen difluorides dissolved in water and aqueous organic solvent mixtures. Accurate binding energies of F^- and Cl^- to a variety of Lewis acids, including oxides, fluorides, oxofluorides and even alkyls, have been measured using ion cyclotron resonance halide exchange equilibrium techniques.[15]

Useful new thermochemical data have been derived for complex anions and their salts. Thermochemical data for the gas-phase interaction of X^-, X = Cl, Br, or I, with SO_2 have been published by Caldwell and Kebarle.[16]



(1)

Anhydrous tetraphenylphosphonium hydrogendifluoride, a soluble and thermally stable reagent, can be used as a powerful source of F^- ion in a variety of organic reactions, see equation (5).[17] Reaction (6) best describes the fluorination of benzyl bromide:

$$1,2\text{-}(NO_2)_2C_6H_4 \xrightarrow[\text{sulpholane}]{Ph_4PHF_2,100°C} 2\text{-}FC_6H_4NO_2 \qquad \ldots(5)$$

$$2Ph_4PHF_2 + PhCH_2Br \xrightarrow[52°C]{MeCN} Ph_4PH_2F_3 + PhCH_2F + PH_4PBr \qquad \ldots(6)$$

the kinetics of (6) are comparable with those of the $KF/PhCH_2Br/$-18-crown-6 reaction.[18] Clark[19] mentions the existence of a third form of Ar_4PF, namely $Ar_4P[Ar_4PF_2]$, in addition to the simple ionic and molecular forms. Reports of coordinated SbF_6 groups appear as crystal structure data for Fe(TPP)SbF_6, TPP = tetraphenylporphyrin,[20] and both crystallographic and dynamic n.m.r. data for $R_3P(CO)_3(NO)W(\mu\text{-}F)SbF_5$.[21]

7.1.3 Interhalogens and Related Species

Well coordinated ab initio electronic structure calculations have been used to investigate the structure of the F_3^- ion.[22] It was predicted to be stable with respect to F^- and F_2 by about 11 kcal mol^{-1}. The centrosymmetric, linear species has the F-F bond length, 1.70Å, significantly greater than in F_2, 1.41Å, and it is postulated that this reduced repulsive π interaction provides a major stabilising influence. A decomposition product of $ClNF_2.AsF_5$ under suitable conditions was found to be $Cl_3^+AsF_6^-$.[23] This was isolated as a blue-green product in the presence of excess Cl_2.

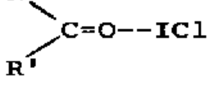
Extensive ab initio calculations have predicted structures and energies for the T-shaped molecules Cl_2F_2, Cl_3F and Cl_4:[24] each is thermodynamically stable with respect to atomisation but not to dissociation into mixtures of ClF and Cl_2, as appropriate. The matrix-isolation technique has been successfully employed for the production of complexes between ClF and a variety of O-containing bases, e.g. Me_2O or ethylene oxide.[25] Twin-jet deposition of the reactants was employed throughout with either Ar or N_2 as matrix material. From the i.r. spectroscopic results obtained it appears that ClF behaves as a medium strength Lewis acid, roughly intermediate in strength between SiF_4 and GeF_4.

Olsson[26] has investigated the formation of the trihalide ions Cl_3, ICl_2^-, I_2Cl^-, and I_3^- in methanol by spectrophotometric and potentiometric methods. The reaction between Br_2 and 1,4-diazobicyclo[2.2.2]octane (DABCO) in CH_2Cl_2 produces a novel complex consisting of a linear chain of three H-bonded DABCO units terminated at each end by a $[Br_3.Br_3.Br]$ counterion, apparently bearing a total formal charge of 3-.[27] Bonding between these chains is through H-bonds to a fourth diprotonated DABCO unit. Several polyhalide anions containing I and Br have been synthesised with 2,2'-bipyridinium as the cation.[28] The crystal structures of three of these have been resolved:

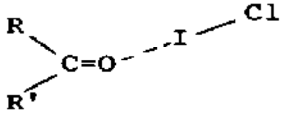
(a) $(bpyH)(H_3O)(IBr_2)_2$, containing two independent, nearly linear, asymmetric IBr_2 ions,

(b) $(bpyH)(I_2Br_3)$, containing a V-shaped pentahalide anion,

(c) $(bpyH)(I_5Br_2)$, in which the polyhalide anion forms infinite zig-zag layers consisting of IBr_2^- ions connected by I_2 molecules.

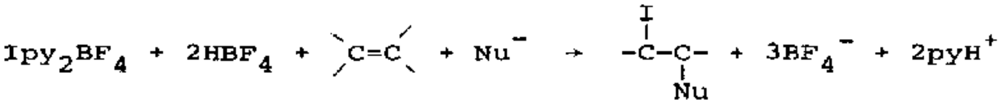


(2)



(3)

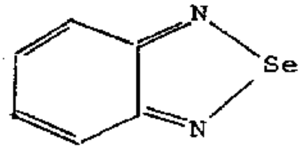
The splitting of the ν(I-Cl) and ν(C=O) bands of ICl complexes with carbonyl bases in dilute heptane solution is explained by the existence of two 1:1 stereoisomeric complexes, (2) and (3), being linear and bent, respectively.[29] Bispyridineiodine(I) tetrafluoroborate, Ipy_2BF_4, reacts with alkenes in the presence of a nucleophile and two moles of acid to form the 1,2-iodo functionalised compound (4), equation (7).[30] The reagent shows a very wide range of generality.



$$Ipy_2BF_4 + 2HBF_4 + \rangle C{=}C\langle + Nu^- \rightarrow -\overset{I}{\overset{|}{C}}-\underset{Nu}{\underset{|}{C}}- + 3BF_4^- + 2pyH^+ \qquad \ldots(7)$$

(4)

Electronic and magnetic circular dichroism spectra of I_3^- have been reported and are consistent with the use of 5p orbitals for the Π_u and Σ_u^+ states of this ion.[31] In an attempted oxidation of 2,1,3-benzoselenadiazol (piaselenol), (5), with iodine a product of composition $(C_6H_4N_2Se)_2H^+I_5^-$ was obtained, the crystal structure of which shows the presence of a layered polyanion comprising I_3^- and I_2 units.[32]



(5)

New complexes of BrF_3 with MF, M = Cs, Rb, have been characterised by Stein[33] and the vibrational spectra reported for $MF.3BrF_3$ and $MF.2BrF_3$. It was also shown that $KBrF_4$ is the only stable solid phase in the KF-BrF_3 system at 23°C. The first example of a stable, but not perfluorinated, arylbromine(III) difluoride has been claimed by Frohn and Giesen:[34] their product contains the p-$CF_3C_6H_4$ as aryl group. A number of alkylphenyliodonium triflates, fluorosulphates and hydrogen sulphates, in which the alkyl group is R_fCH_2, have been prepared in order to compare their stabilities with the R_fCF_2 group.[35]

The standard enthalpies of formation of methyl- and ethylammonium tetrachloroiodates, $(R_nNH_{4-n})(ICl_4)$, R = Me or Et, $0 \le n \le 4$, have been determined by an aqueous solution reaction method using $AgNO_3$.[36] Lattice energies were then calculated and are also presented in Table 2.

Table 2. Standard enthalpies of formation, $\Delta H_f°$ (c), and lattice energies, U, of $NR_nH_{4-n}ICl_4$ (R = Me or Et; $0 \leq n \leq 4$), NH_4ICl_4, and NMe_4ICl_2.

Compound	$-\Delta H_f°$/kJ mol^{-1}	U/kJ mol^{-1}
NH_4ICl_4	415.1 ± 3.6	427
$NMeH_3ICl_4$	420.0[a]	392
$NMe_2H_2ICl_4$	422.6 ± 2.0	375
NMe_3HICl_4	427.6 ± 1.6	357
NMe_4ICl_4	425.7 ± 6.2	
$NEtH_3ICl_4$	450.9 ± 4.5	396
$NEt_2H_2ICl_4$	481.1 ± 4.1	362
NEt_3HICl_4	525.0[a]	360
NEt_4ICl_4	569.4 ± 4.1	
NMe_4ICl_2	357.4 ± 3.0	

[a] Interpolated value.

Chlorine(V) fluoride has been prepared in high purity by the fluorination of ClF_3 at -78°C with O_2F_2.[37] In the presence of a large, 25-fold excess of O_2F_2 the yield is quantitative. Sukhoverkhov and Ellern[38] have studied the solid-liquid equilibria in the MF_5-BF_3, M = Cl or Br, systems by d.t.a.. No chemical compound formation was detected in either system. Iodine pentafluoride in CH_2Cl_2 or MeCN readily converts the triaryls of the elements of group V to the difluorides, equation (8), without causing any significant amount of C-H or C-M cleavage.[39] The adduct $2Ph_3PO.IF_5$ was obtained when Ph_3PO was treated with IF_5. Frohn and Pahlmann[40] have investigated the reactions of IF_5 with a series of α,β-trimethylsilylated ethanediolates. The iodine-containing products obtained included the short-lived

$2IF_5 + 5Ar_3M \rightarrow 5Ar_3MF_2 + I_2$ ...(8)

M = P, As, Sb or Bi

$IF_4[OC_2H_{4-n}Me_nO]X$, X = $SiMe_3$ or IF_4, as well as stable $IF_3[OC_2H_{4-n}Me_nO]$ and $IF[OC_2H_{4-n}Me_nO]_2$, n = 0 to 4.

7.1.4 Oxides, Oxide Halides and Oxoanions

Oxygen difluoride has been shown to fluorinate ClF_3[37] and also hex-1-ene[41] at -78°C in $CFCl_3$. In the latter reaction alkali metal carbonate was added to reduce the extent of polymerisation side reactions; the reaction products were 2-fluorohexanol and hexanone. Ghibaudi et al[42] have reported an extended set of O-F bond energy (D kcal mol^{-1})/^{19}F n.m.r. (ϕ ppm from $CFCl_3$) chemical shift data for fluoroxy compounds. A new non-linear expression, $D = 37.1 + 18.1 \times \tanh[(222.7-\phi)/117.5]$, was proposed. Trifluoromethyl hypofluorite, CF_3OF, reacts quantitatively with ethyl radicals;[43] according to Wang and Rowland the estimated room temperature rate constant is at least 10^{-16} cm^3 $molecule^{-1}$ s^{-1}. Acetyl hypofluorite has been prepared by the passage of dilute F_2 through solid KOAc.2HOAc and isolated by trapping at -78°C.[44] The slightly yellow liquid (m.p. ca. -96°C) has an extrapolated b.p. of 53°C, however the liquid phase is unpredictably explosive. The compound has been characterised by ^{19}F n.m.r. spectroscopy, mass spectrometry, and i.r. spectroscopy of the matrix-isolated material. At room temperature the half-life of the vapour is 2h in Kel-F apparatus; the decomposition products are CH_3F and CO_2. Gas chromatography and n.m.r. spectrosoopy, ^1H and ^{19}F, studies of the oxidising solution obtained by the reaction of F_2 with NaOAc support the view that a compound with the molecular formula CH_3COOF indeed exists.[45]

$2Cl_2 + H_2O + CaCO_3 \rightarrow 2HOCl + CO_2 + CaCl_2$ ...(9)

$Cl_2O + H_2O \rightleftharpoons 2HOCl$ ...(10)

$HOCl + I^- \rightarrow HOI + Cl^-$ ...(11)

A new laboratory source of gaseous hypochlorous acid has been devised;[46] it depends on reaction (9), between Cl_2 and aqueous

$CaCO_3$, and the report describes its use to investigate reactions of HOCl before it equilibrated, equation (10). The equilibrium constant K_{10} was determined in the course of this study to be 0.092 ± 0.011 at 298K. Iodine in the +1 oxidation state was produced either by reaction (11) or (12). Both reactions are rapid and thus Paquette and Ford[47] were able to determine the electronic spectra of OI^-, HOI and its conjugate acid H_2OI^+ in aqueous media. They proceeded then to obtain evidence for the disproportionation of $OI^-/HOI/H_2IO^+$ to iodide and iodate in basic media, and to iodine and iodate in acid media. Jenkin and Cox have used a photochemical modulation technique to study reactions of the IO· radical such as (13) and (14) as well as the complex reaction between two IO· radicals.[48]

$$ICl(gas) + H_2O \rightarrow HOI + Cl^- + H^+ \qquad ...(12)$$

$$IO\cdot + NO_2 + M \rightarrow IONO_2 + M \qquad ...(13)$$

$$I + O_3 \rightarrow IO\cdot + O_2 \qquad ...(14)$$

$$ClO_2^- + 4H^+ + 4Br^- \rightarrow Cl^- + 2Br_2 + 2H_2O \qquad ...(15)$$

A kinetic study of reaction (15) has revealed two distinct pathways:[49] the rate expression (16) has $k_1 = (1.39 \pm 0.05) \times 10^{-1}$ $M^{-2}\ s^{-1}$ at 25°C in 0.5M $LiClO_4$ solution, whereas at low $[Br^-]$ the reaction has an induction period. Alamgir and Epstein have reported sustained oscillations in their study of the reactions

$$\tfrac{1}{2}d[Br_2]/dt = k_1[ClO_2^-][H^+][Br^-] + k_2[ClO_2^-][Br_2]/[Br^-] \qquad ...(16)$$

between ClO_2^- and either Br^- or NCS^- in stirred tanks.[50] The disproportionation of ClO_2^- in 0.01 to 1M perchloric acid at 25°C appears to have at least three reaction paths.[51] The first is catalysed by Cl^- ions, another gives a second order rate law, and the third is catalysed by iron, equation (17). The latter can be interpreted by reaction (18), followed by two competing, rate-determining steps in which Fe^{2+} reduces either ClO_2^- or $HClO_2$ to give the products.

$$d[ClO_2]/dt = [Fe^{3+}][ClO_2^-][HClO_2](1.39 + 0.11/[H^+])/[ClO_2] \qquad ...(17)$$

$$ClO_2^- + Fe^{3+} \rightleftharpoons ClO_2 + Fe^{2+} \qquad ...(18)$$

Codeposition of MeI and ozone in excess Ar at 17K leads to the formation of a molecular complex which photodissociates (360-470nm) to iodosomethane, MeIO.[52] Further photolytic rearrangement of this gives iodomethanol, ICH_2OH, methyl hypoiodite, MeOI, and formaldehyde. Using trifluoromethyl iodide instead of MeI a complex $CF_3I.O_3$ is formed which forms CF_3IO on photolysis (470-1000nm).[53] Further irradiation (240-420nm) produces CF_3OI and two CF_2O--IF molecular complexes. The reaction of elemental iodine with ozone in the gas phase (100kPa) over the temperature range 293-370K produces a solid iodine oxide of composition I_4O_9.[54] The observed kinetics suggest that the rate determining step is a bimolecular reaction to form I, IO and IO_2. The reaction rate and product stability are suitable for the basis of a method for removing radioiodine from air in a nuclear facility.

Single crystals of the anhydrous halates $Ba(BrO_3)_2$, $M(BrO_3)_2$, and $M(ClO_3)_2$, M = Sr, Pb, have been obtained and the crystal structures of both Sr compounds determined.[55] The action of Cl_2O_6 on metal chlorides or nitrates yields anhydrous $M(ClO_4)_2$, M = Co, Ni, Cu, and their chloryl, ClO_2^+, or nitryl, NO_2^+, salts.[56] Potier et al. were able to make anhydrous perchlorates and perchlorato complexes for In and Tl(III) similarly.[57] They characterised the products by vibrational spectroscopy and X-ray powder diffraction. The reaction of dichlorine heptoxide with N,N'-disubstituted diamines has produced three new compounds, e.g. $O_3ClNMeCH_2CH_2NMeClO_3$, each containing two perchloryl groups.[58] On account of the explosive tendencies of the products they were characterised in solution by i.r. and ^1H n.m.r. spectroscopy. Anhydrous niobium(V) perchlorate has been prepared from $NbCl_5$ and $HClO_4/Cl_2O_7$:[59] it is a hygroscopic solid which decomposes at 70°C to $NbO(ClO_4)_3$ and Cl_2O_7. Caesium salts of $Nb(ClO_4)_6^-$ and $Nb(ClO_4)_7^{2-}$ were also reported. The action of heat on $Cs_n[Hf(ClO_4)_{n+4}]$, n = 1, 2, or 3, has been studied by d.t.a., X-ray diffraction and i.r. spectroscopy.[60] When n = 1 the decomposition occurs according to the nearly quantitative reaction (19), on account of the volatile nature of $Hf(ClO_4)_4$. The densities of various metal perchlorates have been measured pyknometrically:[61] the packing density of oxygen in the salts of the lighter metals is higher than that in liquid oxygen itself.

$$2Cs[Hf(ClO_4)_5] \rightarrow Cs_2[Hf(ClO_4)_6] + Hf(ClO_4)_4 \qquad ...(19)$$

Carbon monoxide in the presence of $Pd_3(OAc)_6$ causes the catalytic reduction of perchloric and periodic acids to the halide ions.[62] Stable oxygen-bonded derivatives of Xe(II) and Xe(IV) with the highly electronegative $-OIF_4O$ group have been prepared by reactions of xenon compounds with $(IO_2F_3)_2$ or $HOIOF_4$.[63] Xenon-129 n.m.r. chemical shifts were used to establish $-OIF_4O$ as the most electronegative group known next to fluorine.

7.1.5 Hydrogen Halides

O'Donnell has reported on the progress in exploiting the chemistry of Lewis acids in anhydrous fluoride.[64] Tetra-n-butylammonium and polymer-supported dihydrogen trifluoride have been shown to effect HF addition to activated $-C{\equiv}C-$ bonds to form $-CH{=}CF-$containing products.[65] The structures, association energies and vibrational frequencies of $(HF)_2$ and $(HCl)_2$ have been reinvestigated at a consistent, higher level of theory. Data for the monoprotonated $(HX)_2H^+$ were also presented.[66]

7.2 HYDROGEN

7.2.1 The Element

Theoretical investigation of reaction (20) and of the FH_2 potential energy hypersurface has been reviewed by Schaefer,[67] who draws attention to the importance of zero-point vibrational and tunnelling corrections in making reliable predictions of the activation energy for this reaction. Clark and coworkers[68]

$$F + H_2 \rightarrow FH + H \qquad ...(20)$$

remind us that Raman spectroscopy is a sensitive technique for the detection of submicromolar quantities of gaseous H_2 (HD or D_2) owing to the favourable scattering cross section of H_2.

7.2.2 Protonic Acids and Hydrogen-Bonding

Pulsed electron beam high pressure mass spectrometric techniques have been used to study proton transfer equilibria involving compounds less basic than H_2O.[69] The results obtained allowed McMahon and Kebarle to construct a continuous scale of gas-phase affinities from CH_4 (134.7kcal mol^{-1}) upwards. An excellent correlation between the gas-phase proton affinity of oxygen bases and the corresponding oxygen 1s binding energies obtained from ESCA experiments was obtained, see Figure 2. Experimental measurements of the gas-phase ion equilibria (21) and (22), where X,Y = Cl, Br or I, with a high pressure mass spectrometer, complement the data for X = Y = F and provide a

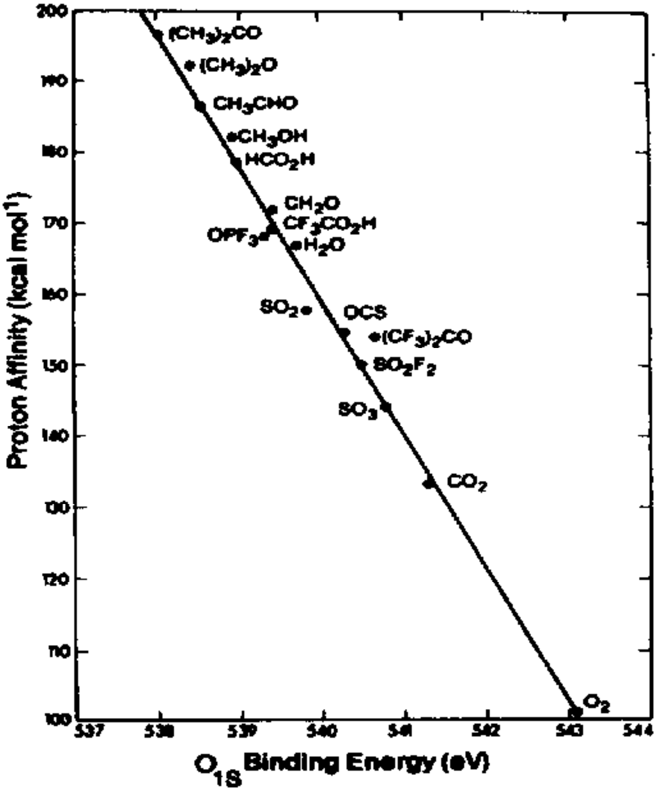


Figure 2. Variation of proton affinities of oxygen bases as a function of O1s binding energy (reproduced by permission from J. Am. Chem. Soc., 107(1985)2612).

$$X^- + HY \rightleftharpoons XHY^- \qquad ...(21)$$

$$X^-(HX)_{n-1} + HX \rightleftharpoons X^-(HX)_n \qquad ...(22)$$

complete set of H-bond dissociation enthalpies, see Table 3, and free energies for the XHY^- ions.[16] The experimental determination of the hydrogen bond energy of the HF_2^- ion has made possible accurate lattice energy calculations of the alkali metal bifluorides, $U(MHF_2)$, see Table 4. Emsley[70] has proceeded to make estimates of the lattice energies of NH_4HF_2 and the alkaline earth bifluorides.

Table 3. Hydrogen bond cleavage enthalpy (kcal mol^{-1}) change; $(XHY)^- \rightarrow X^- + HY$ and $(XHY)^- \rightarrow Y^- + HX$.

	Enthalpy change for HY =			
X^-	HF	HCl	HBr	HI
F^-	38.6	59.9	(65.0)	(72.0)
Cl^-	21.8	23.5	29.4	30.7
Br^-	(17.0)	19.6	20.9	25.4
I^-	(15.0)	14.4	16.1	17.0

Table 4. Lattice energies of the alkali metal bifluorides, $U(MHF_2)$ (all energies in kJ mol^{-1}; 298.15K)

	Li	Na	K	Rb	Cs
$-\Delta H_f^{\ominus}(MHF_2)(s)$	923.9	906.2	920.4	909.2	904.2
$-\Delta H_f^{\ominus}(MF)(s)$	611.7	569.0	562.8	551.5	545.2
U(MF)	1025	903.7	801.2	768.1	715.5
$U(MHF_2)$	903	807	725	692	640
ΔU†	122	97	76	76	75

† $\Delta U = U(MF) - U(MHF_2)$.

The dissociation energies of complexes $RCNH^+$--B or BH^+--NCR, B = R_3N, RCN, O-bases, show an inverse linear correlation with proton affinity differences of the components.[71] The variation of the correlation parameters with dipole moment of the ligands and with the charge density of the bonding was justified by electrostatic calculations. This study was extended to cover SH^+--O and NH^+--S interactions in a subsequent paper.[72] Evidence for unconventional hydrogen bonds between C and C, O, or N has been reported in a study of the clustering of quaternary 'onium ions with a variety of n- and π-donors, such as MeOH and benzene, respectively.[73] Thus the dissociation energies of the 1:1 complexes involving Me_4N^+ were found to lie mainly in the range 8 to 10 kcal mol^{-1}. Ab initio calculations showed that the donor atom in $Me_4N^+.D$, D = H_2O, MeOH, $MeNH_2$ and MeCl, complexes attaches itself electrostatically to a cavity between the protons of three Me groups, rather than to one proton or, even, one Me group. Both experiment and theory indicate that a second solvent (base) molecule attaches itself to the first one in the 1:2 adducts. Other unconventional and stronger hydrogen bonds of the XH^+--(π-donor) type are formed in the clustering reactions of NH_4^+ and $MeNH_3^+$ with C_2H_4 and benzene derivatives:[74] interaction energies fall in the range 10 to 22 kcal mol^{-1}.

Infrared radiation dissociates the strongly H-bonded dimethylacetamide-HI complex in Ar matrices to form a weakly H-bonded complex;[75] this process was found to be reversed when the matrix was briefly warmed to ca. 35K. 1,2,3-Benzotriazole and H_3PO_4 produce crystals of a 1:1 adduct, whose structure contains very short NHO (2.61 and 2.66Å) and OHO (2.45 and 2.48Å) hydrogen bonds.[76]

7.2.3 Hydrides and Dihydrogen as a Ligand

1,8-Naphthalenediylbis(dimethylborane) (1) has been synthesised and shows a high affinity for anions, especially H^-.[13] The crystal structure of KH.(1).(dioxane)$_3$ reveals a B-H-B bridge angle of 142° with B-H distances of 1.29(5) and 1.49(5)Å. The complex was found to be kinetically stable with respect to benzaldehyde in dioxane (18h/60°C). An analysis by Squires[77] of recently determined diatomic metal hydride bond energies and metal atom electron affinities shows the following trends:

(a) diatomic MH gas-phase acidity is generally constant and equal to 341 ± 5 kcal mol^{-1},

(b) a simple linear relationship exists between metal atom electron affinity and M-H bond dissociation energy, namely $D(M\text{-}H) = EA(M) + 27.5(\text{kcal mol}^{-1})$.

Infrared bands due to the dissociative adsorption of H_2 (27-53 kPa) on to ZrO_2 at room temperature have been detected by the f.t. method;[78] ν(Zr-H) and δ(Zr_2H) were assigned to bands at 1562 and 1371 cm^{-1}, respectively.

The photochemical generation of [$Cr(CO)_5H_2$] from $Cr(CO)_6$ and H_2 in solution has been reported by two groups of workers.[79,80] The Nottingham group[79] carried out the photolysis in liquid xenon at 200K and showed that coordinated H_2 has an i.r. band at 3030 cm^{-1} Both groups identified the same material as the product of photolysis of $Cr(CO)_6$ and H_2 in hydrocarbon solvents at room temperature. Crabtree and Lavin[81] have questioned whether the classical formulation of polyhydride complexes as MH_xL_y, containing terminal M-H groups only, is always valid. They have now shown that [$IrH_2(bq)(PPh_3)_2$], Hbq = benzo[h]quinoline, and [IrH_5L_2], L = Pcy_3, may be protonated to give the dihydrogen hydride cations, $[IrH(H_2)(bq)(PPh_3)_2]^+$ and $[IrH_2(H_2)_2L_2]^+$, respectively. Both cations tend to lose H_2 at room temperature; indeed MeCN displaces $2H_2$ form the latter to give $[IrH_2(MeCN)_2L_2]^+$.

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