Coordination Chemistry Reviews, 66 (1985) 488—503
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 7

THE HALOGENS AND HYDROGEN

M.F.A.Dove

7.1 THE HALOGENS

7.1.1 The Elements

Progress in electrochemical fluorination has been reviewed by Watanabe:[1] extensive tabulations of ^{19}F n.m.r. data covering the period 1979-1981 have appeared in a recent report by Wray.[2]

Jolly and Eyermann[3] have presented interesting evidence for the unusually strong lone pair interatomic repulsions in F_2. The relevant data for the halogens and the diatonic interhalogens are shown in Table 1.

Table 1. LOIPs, Ionization Potentials, and Δ Values for Halogens and Interhalogens (eV)

molecule	LOIP	IP(π)	IP(π*)	Δ
F_2	17.94	18.80	15.84	-0.62
Cl_2	13.12	14.42	11.61	-0.10
Br_2	11.85	12.85	10.68	-0.08
I_2	10.35	11.21	9.51	0.01
ClF	15.09	17.06	12.79	-0.16
ICl	11.56	12.88	10.24	0.0
IBr	10.59	12.09	9.99	0.45

0010-8545/85/$05.60

The value of Δ in this Table is equal to $(IP(\pi) + IP(\pi^*))/2 - LOIP$, where $IP(\pi)$ and $IP(\pi^*)$ are, respectively, the π and π^* ionisation potentials and LOIP is the localised orbital ionisation potential for the valence p orbitals if they were non-bonding (or the average value for heterodiatomics). Christe[4] has criticised the views, proposed by Cartwright and Woolf and others, that positive fluorine is a reality.

The attack of F atoms on MeI molecules occurs to a small extent by reaction (1);[5] it is possible that this process is accompanied

$$F + MeI \rightarrow CH_3F + I \qquad \ldots(1)$$

by an inversion at C. The reactions of F_2 with the phenyl derivatives of Sn, Pb, Ge, Si, Hg and Tl have been studied in order to develop a general method for labelling aromatic compounds with ^{18}F.[6] Chemical yields were as high as 70% from certain tin compounds, although the radiochemical yield was only 38%. Several hundred millicuries of $^{18}F-F_2$ can be produced with a small medical cyclotron using deuteron irradiation of a mixture of 0.5% F_2 in Ne at an initial pressure of 4 atm.[7]

The low temperature fluorination of R_2Hg (R = Me, Ph) in $CFCl_3$ with diluted F_2 provides good yields, 26 and 40% respectively, of MeHgF and PhHgF.[8] 15-Difluoroaminopentadecanoic and 12-difluorododecanoic acids have been prepared by direct fluorination of the corresponding lactams with F_2 in aqueous MeCN.[9] The NF_2-group stability in aqueous solution was studied as a function of pH and the advantages of using CH_2NF_2-groups rather than CH_2F-groups as labels in organic compounds were stressed.

Fluorine interacts with graphite in the presence of liquid HF and intercalation occurs with the formation of the second-stage salt $C_{12}{}^+HF_2{}^-$ within 2h at 20°C.[10] Further reaction produces a first-stage material C_xF ($5.4 > x > 1.9$) which is essentially free of HF. Electrochemical reduction of first-stage materials having $x > 2.4$ was also demonstrated by Mallouk and Bartlett and, conversely, electrochemical oxidation of graphite could be effected through to a first-stage compound having a minimum value of $x \simeq 2.6$. Selig and coworkers[11] have demonstrated that pure F_2 does react with highly oriented pyrolytic graphite (HOPG) albeit slowly: the rate was shown to increase with increasing F_2 pressure. The presence of traces of compounds such as AsF_5, IF_5 and OsF_6 was found to enhance the rate of reaction. The products of intercalation were significantly better basal plane conductors than those obtained by Mallouk and Bartlett. Interestingly the room temperature e.s.r. signals from HOPG and from the initial reaction product may be used to detect the onset of reaction.

Through the nuclear radiative time-dependent angular distribution (DPAD) technique an increasing amount of nuclear quadrupolar interaction data is being obtained for the τ = 129ns isomeric state of the excited, $I = {}^5/2$ state of the ^{19}F nucleus.[12] Both the quadrupole coupling constants and asymmetry parameters in fluorine compounds are thus measurable: recently data have been reported for a number of fluorobenzenes.

The solubility of Cl_2 in molten NaCl, in NaCl-CsCl eutectic and in chloroaluminate melts has been determined by a manometric method.[13] Asymmetric chlorination or bromination of unsaturated carboxylic acids has been achieved by the action of the halogen on the crystalline cyclodextrin complex of the acid.[14] It was established that the gas-solid reaction is topochemically controlled by the lattice of the complex. MNDO calculations have been used to throw light on the nature of the reaction of Cl_2 with H_2O_2 in basic media in which $O_2(^1\Delta)$ is the principal product of interest.[15]

7.1.2 Halides

The linewidths of the F 1s X-ray p.e.s. of the binary noble gas fluorides and of other fluorinated compounds have been shown to be due to vibrational broadening and not, in the case of XeF_6, to inequivalent fluorines.[16] The ^{19}F MAS-NMR spectra at 282.3MHz of synthetic fluoroapatite, $Ca_5F(PO_4)_3$, and of fluoridated hydroxyapatite probe all the fluoride present for crystalline and amorphous samples whether the fluoride is adsorbed or not.[17] The appearance of the spectra is, however, very sensitive to the form of F^-.

The reaction of CsF with SO_2 in an Ar matrix produces a species with absorptions characteristic of the SO_2F^- anion.[18] The analogous reactions with SOF_2 and SO_2F_2 yielded SOF_3^- (C_s geometry) and $SO_2F_3^-$, with a structure related to that of ClO_2F_3. Attina et al.[19] have demonstrated that activated nitro-groups can be displaced efficiently by [^{18}F] fluoride ion to prepare labelled aryl fluorides. Solvent-free phase transfer catalytic fluorinations of aliphatic chlorides or bromides by KF have been described:[20] the water content of the KF and breakdown of the catalyst, e.g. a quaternary ammonium or phosphonium salt, have a major effect on the yields. Brown and Clark[21] have prepared an ionic and a covalent form of Ph_4PF from the HF_2^- salt.

An unusual trinuclear complex $Ph_3C^+[(Ph_3CNWCl_4(\mu\text{-}F))_2WNCl_2]^-$ is the product of reaction of Ph_3CBF_4 with $Ph_4As[WNCl_4]$ and has been shown by X-ray methods to contain unsymmetrical W-F---W bridges.[22] The MoFMo bridges in $[Mo_2(\mu\text{-}F)_3H_4(PMePh_2)_6](BF_4)_2$ were found to have angles of about 98°.[23] Ion cyclotron resonance F^--transfer equilibrium measurements have been carried out with a wide range of Brønsted acids;[24] accurate binding energies of F^- to these species were obtained, e.g. in HF_2^-, 38.6 kcal. mol^{-1}. Within a homologous series of acids the correlation of gas phase acidity with fluoride ion affinity is quite clear, Figure 1. Ault[25] has discussed the chloride and fluoride ion affinities of neutral species, as determined by gas phase ion cyclotron resonance studies, with those calculated for a number of M^+ cations, Table 2. He points out that there must be strong ion pair interactions in matrix-isolated species formed by salt-molecule reactions to

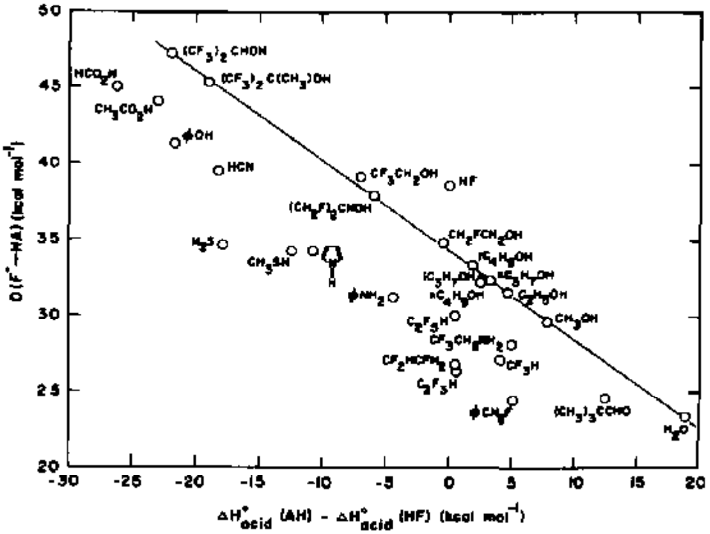


Figure 1. Correlation of fluoride binding energies with gas phase acidity of Brønsted acids (reproduced by permission from J. Am. Chem. Soc., 105(1983)2944).

Table 2. Halide Ion Affinities of Alkali-Metal Cations and Selected Neutral Lewis Acids.[25]

Cation	FA, kcal/mol	CA, kcal/mol	Lewis acid	FA, kcal/mol
Li^+	180.5	150	HF	50
Na^+	151	130	SiF_4	68
K^+	136	115	BF_3	71
Rb^+	131	110	COF_2	34
Cs^+	128	110	CO_2	32
Tl^+	162	148	SO_2F_2	43
Cu^+	186	179.7	PF_5	71

counterbalance the disparate values for the tabulated affinities. These interactions are presumably the origin of the distortions of the anionic species reported in the literature.

Chloride anion complexes formed by some protonated cryptands, macrobi- and macro-tricyclic polyammonium species, have been studied by Cl, ^1H and ^{13}C n.m.r. spectroscopy.[26] Kintzinger et al. showed that cryptate formation induces very large chemical shifts and pointed out that the quadrupolar coupling constants are consistent with appreciable field gradients at Cl^- due to deformation of the coordination shell. The I--I contacts reported by Pohl[27] for $PI_4^+AlI_4^-$ (3.39-3.45Å) and $P_2I_5^+AlI_4^-$ (3.43-3.76Å) are significantly shorter than the sum of the van der Waals' radii (4.30Å). The partial oxidation of [PtdienCl]Cl with I_2 in aqueous HI yields $[PtdienI]^+[Ptdien(I)_3]^+(I^-)_2$ as bronze crystals.[28] The structure of the product has well-defined Pt(II) and Pt(IV) sites linked by bent iodine bridges, angles 153° and 158°. Certain Pd(II) iodide complexes react with I_2 to form adducts in which coordinated iodines on adjacent Pd(II) molecules are linked by I_2 molecules;[29] this is in contrast with the behaviour of the analogous chlorides and bromides which tend to form Pd(IV) complexes.

7.1.3 Interhalogens and Related Species

Stable cationic complexes of At^+ with thiourea and related ligands have been investigated in aqueous solution by measurement of their ionic mobilities.[30] The complex claimed by Batsanov et al.[31a] to be $[ClF_6][CuF_4]$ is now thought to be

$[Cu(H_2O)_4]SiF_6$.[31b] The molecular ions of the methyl esters of chloro-, bromo-, dichloro- and dibromo-acetic acids undergo unimolecular elimination of CO_2 in the gas phase.[32] Novel types of hypervalent structures, e.g. $MeXCH_2^+$ and $MeXCHX^+$, X = Cl,Br, are proposed for the resulting radical ions and their relative stabilities have been estimated by calculations. MNDO calculations have been reported for a wide range of triatomic and diatomic species containing F, Cl, O and H.[33] Amongst the most stable isomers predicted were $ClClF^+$, $FClF^+$ and $HFCl^+$.

Studies of the reactivity of ClF_3, BrF_3 and BrF_5 with perfluorinated aromatic hydrocarbons have shown that the interhalogens are more reactive in the presence of F^- ion acceptors.[34] The 1:1 adduct of ClF_3 with BiF_5 has been recently described:[35] it was reported to ionise in MeCN to give ClF_2^+.[36] Christe and Wilson[37] have successfully prepared the BF_4^- salt of ClF_6^+ by reaction (2) in anhydrous HF. This new salt is stable

$$ClF_6AsF_6 + CsBF_4 \xrightarrow{-78^{\circ}C} CsAsF_6\downarrow + ClF_6BF_4 \qquad ...(2)$$

at room temperature but decomposes in vacuo at ca. 70°C. The hexafluoroarsenate is produced in good purity by the oxidation of ClF_5 and AsF_5 with KrF_2 in either ClF_5 or HF:[38] it is stable up to 110°C in a dynamic vacuum and is isotypic with IF_6AsF_6. On the other hand the analogous reaction of KrF_2,ClF_5 and SbF_5 produces not only ClF_6SbF_6 but also ClF_4SbF_6 and $KrF_2.nSbF_5$.

Bis(quinuclidine)bromine(I), a stable complex cation, has been prepared as its BF_4^- salt and the structure determined.[39] The cation has a linear N-Br-N arrangement but with unequal Br-N distances, 2.156(2) and 2.120(2)Å, in this salt. The action of $BrSO_3F$ on graphite yields a series of intercalation compounds.[40] Oxidation of $C_{12}BrSO_3F$ with $S_2O_6F_2$ produces $C_{16}Br(SO_3F)_3$ but the reaction may be reversed by treatment with excess Br_2. The reaction of NF_4SbF_6 with excess BrF_3 cannot be used to obtain satisfactory thermochemical data owing to the occurrence of unwanted side reactions.[41]

The I_4^{2+} cation has been fully characterised for the first time by the preparation of the compounds $I_4(AsF_6)_2$ and $I_4(Sb_3F_{14})(SbF_6)$ and the determination of their crystal structures.[42] The I_4^{2+} ion has a rectangular structure and may be considered to consist of two I_2^+ cations, average I-I = 2.578Å, held together by two long, 3.264Å, interactions. The crystal lattice of Co(NH$_3$)$_6$I$_7$ is comprised of nearly octahedral Co(NH$_3$)$_6^{3+}$, linear symmetric I$_3^-$, and slightly bent, but symmetrical I$_4^{2-}$ ions; the I-I distances in I$_4^{2-}$ are 3.351(1)(twice) and 2.791(2)Å, as compared with 2.918Å in I$_3^-$.[43] The Pd(II) and Pt(II) complexes of the macrocycle tetrabenzotetraazacyclohexadecine, TAAB, both stabilise lattices containing the I$_8^{2-}$ dianion. Attempts to prepare the Ni(II) analogue failed when MeCN was the solvent: the product obtained was [Ni(TAAB)(MeCN)$_2$](I$_3$)$_2$, the crystal structure of which has now been reported to help identify the role that the cation coordination plays in modifying the anion stability.[44] These workers, however, did succeed in preparing [Ni(TAAB)]I$_8$ from ethanol solutions.

Winfield and coworkers[45] have shown that I$_2$ is oxidised by MoF$_6$ in MeCN at ambient temperatures to form [I(MeCN)$_2$]MoF$_6$. Accurately reproducible coulometric titrations involving the oxidation of I$_2$ to IBr$_2^-$ in 4M HBr have been carried out using an iridium anode.[46] The same worker proposed an improved procedure for the purification of I$_2$ which is based on the precipitation of I$_2$ from saturated 10M HI-I$_2$ solutions by the addition of water. The X-ray crystal structures of [IBr$_2$][Sb$_2$F$_{11}$] and [IBr$_{0.75}$Cl$_{1.25}$][SbCl$_6$] have been determined.[47] Both structures consist of infinite chains of cations and anions such that the iodine in each cation achieves a trapezoidal four-coordination via cis bridges to the anions. The symmetric stretching vibrations of I$_3^-$, I$_2$Cl$^-$ and ICl$_2^-$, as well as of an unidentified higher polyiodide ion, have been observed in the Raman spectra of molten LiCl-CsCl and LiI-CsI eutectics at 300-400°C.[48] The crystal structure of (2,2'-dipyridyl)$_2\overset{+}{I}$N$_3^-$ shows a linear N-I-N arrangement in the cationic species.[49]

Tebbe and Fröhlich[50] have attempted unsuccessfully to repeat the published preparation of MI(CN)$_2$, M = alkali metal; however, after 6 weeks the reaction of KCN and ICN in aqueous EtOH at 255K yielded crystals of KI(CN)$_2$.C$_6$H$_{12}$N$_2$O$_2$. The same compound was prepared more directly from KCN, ICN, and diiminooxalic acid dimethyl ester, C$_6$H$_{12}$N$_2$O$_2$. The new compound contains the nearly linear I(CN)$_2^-$ anion (I-C = 2.302Å) and octahedrally coordinated K$^+$ ions. The molecular structure of monomeric (indolyl-3)phenyliodonium trifluoroacetate consists of a unidentate carboxylato ligand trans to the carbon atom of the indolyl group (I-C =

2.047Å); the phenyl group is equatorial (I-C = 2.128Å).[51] Phenyliodine(III) bisimidates have been prepared by reactions like (3), where NR_2^- represents the anion derived from a range of

$$PhI(OCOCF_3)_2 + 2NaNR_2 \rightarrow PhI(NR_2)_2 + 2CF_3CO_2Na \qquad ...(3)$$

heterocyclic compounds with an acidic NH group, such as isatin or 2-pyridone, but not from non-cyclic imides, e.g. $(CF_3CO)_2NH$.[52] Diphenyliodonium hexafluoroarsenate reacts with Cu(II) benzoate in methanol to give mainly PhI and MeOPh.[53] When Ph_2IBr replaces the AsF_6^- salt then PhBr is also formed. The heats of formation of $PhICl_2$ and $p\text{-}FC_6H_4ICl_2$ have been determined by Cartwright and Woolf.[54] They could also show that the thermal- or photo-decomposition of aryliodine dichlorides are kinetically controlled and that these compounds are better halogenating agents than Ph_3MCl_2 (M = P, As or Sb). The reaction of $PhICl_2$ with silver 4-nitrophenolate is quantitative, equation (4), however attempts

$$PhICl_2 + 2AgOC_6H_4NO_2 \rightarrow PhI(OC_6H_4NO_2)_2 + 2AgCl \qquad ...(4)$$

to isolate the iodine(III) diphenolate produced only PhI and 4-nitrophenol.[55] The ^{127}I Mössbauer spectra of a number of iodine(III) cations and related species, having four ligands and two non-bonding electron pairs around I, have been recorded.[56] The Mössbauer parameters are dominated by the primary bonding to iodine.

Iodine(V) fluoride can be mono-substituted by oxo groups using silylated alcohols, carboxylates or siloxane itself to give stable products.[57] Further substitution gives rise to unstable products.

7.1.4 Oxides, Oxide Halides and Oxoanions

Shreeve[58] has reviewed the chemistry of fluorinated hypofluorites and hypochlorites. A new method for the synthesis of hypofluorites has been described.[59] The method involves the use of $FOSO_2F$ and is typified by the high yield synthesis of the new hypofluorite TeF_5OF, reaction (5). Perfluoroalkylhypofluorites react with difluoroamines in the presence of alkali metal

$$CsOTeF_5 + FOSO_2F \rightarrow CsSO_3F + TeF_5OF \qquad ...(5)$$

$$R_fOF + MF.HNF_2 \xrightarrow{-142 \text{ to } -78^{\circ}} R_fONF_2 + MF.HF \qquad ...(6)$$

fluorides (MF), equation (6), to produce the corresponding $-ONF_2$ substituted perfluoroalkanes.[60] This method has been used to prepare the known CF_3ONF_2, $(CF_3)_2CFONF_2$, and unknown $FOCF_2ONF_2$ and $CF_2(ONF_2)_2$, both of which are stable at ambient temperatures.

New far-i.r. laser magnetic resonance spectra have been detected in the reactions of F atoms with O_2 and O_3.[61] These are assigned to the $\cdot O_2F$ radical on the basis of chemical and kinetic results and also qualitative spectroscopy. The thermal decomposition of O_2SbF_6, a known source of $\cdot O_2F$, also yielded the same spectra. The Ar matrix-isolated products of reaction of F atoms and methyl nitrite show characteristic i.r. bands of FNO and another species FON.[62] Ethyl iodide is fluorinated by a suspension of $CsSO_4F$ in MeCN with the formation of $EtIF_2$, detected by the products of its reaction with $PhC{=}CH_2$.[63] The reaction of HOCl and $NHCl_2$ is general base catalysed.[64] Since NCl_3, formed in this way, reacts with $NHCl_2$ to generate more HOCl the rate of decomposition of $NHCl_2$ is accelerated.

The i.r. spectrum of matrix-isolated chlorine nitrate shows absorptions which may be associated with both $ClONO_2$ and ClOONO:[65] assignment of the spectrum of the peroxy-isomer was reported. Inorganic hypochlorite ions, in the presence of a quaternary ammonium salt (as phase transfer catalyst), not only epoxidise several arenes to arene oxides in high yield but also convert toluene to α-chlorotoluene.[66] The study, by Hamilton and coworkers, concludes that the reactions occur by a free-radical mechanism involving Cl_2O and the ClO· radical. Schardt and Hill[67] have reported a new synthesis of $[^{18}O]$-iodosylbenzene as well as corrections to the i.r. spectrum of this compound. They stressed its polymeric nature, a fact not recognised by many workers, and that its solubility in, for example, MeOH is due to methanolysis and the formation of bis(methoxy)iodobenzene, equation (7).

$$\frac{1}{n}(PhIO)_n + 2MeOH \underset{H_2O}{\overset{desiccant}{\rightleftharpoons}} PhI(OMe)_2 + H_2O \qquad ...(7)$$

Although a direct exchange of oxygen between PhIO and H_2O does not appear to occur in aqueous solution labelling is facile in the presence of methanol.

The properties of ClO_2 have been reviewed by Masschelein.[68] The non-photochemical reaction of O_2/O_3 with Cl_2 from -78° to -40°C gives $Cl(ClO_3)$.[69] Traces of water lead to the formation of ClO_2 as well as $HClO_3$, HCl and small amounts of other chlorine oxides. The gas phase reaction of pure O_3 and Cl_2 at 15°C and 3atm. yields ClO_2 as well as $Cl(ClO_3)$ and some $Cl(ClO_4)$. I.r. spectroscopy has been used to study alkali metal chlorates in N_2- or Ar-matrices. Beattie and Parkinson[70] have shown that there is a C_3 axis in molecular $CsClO_3$, isolated in an Ar matrix, and have inferred that ClO_3 functions as a tridentate ligand towards Cs.

Perchlorate and perbromate ions are partially protonated in anhydrous HF;[71] the Raman spectra of such solutions show bands attributable both to the anions and to the conjugate acids. From this study it was deduced that $HBrO_4$ is 6 times more acidic than $HClO_4$. Perchlorate coordinated to the Mg(II) centre has been reported for the Mg(5,10,15,20-tetraphenylporphinato) radical cation complex, $Mg(TPP)^{+\cdot}ClO_4^-$.[72] The relevant Mg-O distances (2.012Å) is comparable with that (2.029Å) in $Fe^{III}(TPP)^+ClO_4^-$ and the distances in a number of related species. The kinetics of reaction (8) have been studied in aqueous MeOH and MeCN.[73] Although the oxidation of Cl^- and Br^- by ClO_3F does not proceed

$$ClO_3F + 2I^- \rightarrow F^- + ClO_3^- + I_2 \qquad \ldots(8)$$

in aqueous solution according to Cady the oxidation has been shown to occur in certain other solvents, e.g. MeCN or DMF. The uncontrolled reaction between IO_2F_3 and XeF_2 leads to $XeF_2.IF_5$, IO_2F and O_2; however, at lower temperatures evidence for adduct formation has been studied.[74] The formulation of these adducts has not been satisfactorily settled.

7.1.5 Hydrogen Halides and Hydrogen Bonding

The co-condensation reaction between HF and HCN produces two 1:1 H-bonded complexes in an Ar matrix at 12K.[75] The less stable of these, HF---HCN, is non-linear and isomerises when the matrix is warmed to linear HCN---HF. The corresponding reaction between HCl and HCN yields only the linear analogue. Under similar conditions MeCN forms a 1:1 linear H-bonded complex with HF.[76] Above 20K HF diffusion occurs and MeCN.nHF, n = 2 or 3, are produced. When HCl is used instead of HF both 1:1 and 1:2 adducts were detected.

STO-3G and extended basis set calculations have been performed on the SO_2-HF complex:[77] the results indicate that this should be classed as a H-bonded complex.

Hass and coworkers[78] have investigated the kinetics of the reaction between gaseous HF and solid $CaCO_3$. Pyridinium fluoride hydrofluoride, e.g. py:HF = 3:8, has been used to fluorinate POX_3, PSX_3 and PX_5, X = Cl or Br, to form $pyH^+PF_6^-$.[79] The behaviour of carbon anodes in molten KF.2HF has been studied electrochemically;[80] the results were said to be consistent with the formation of an insulating layer of solid carbon-fluorine compounds. Equilibrium vapour pressures of HF over $BaHF_3$ and MHF_2, M = Na, K or Cs, have been measured in the range 0.01 to 1000Pa.[81] The data were used to derive ΔH_f^o values for the HF solvates. The nature of solutions of KF and KHF_2 in the HF-H_2O system has been reinvestigated by electrical conductivity.[82] The same group have also measured the enthalpies of solution of NH_4F,[82] NH_4HF_2,[82] $NaHF_2$[83] and KHF_2[83] and hence derived the enthalpies of formation of the solid phases.

Asymmetric hydrobromination of unsaturated carboxylic acids has been effected by the action of HBr on the crystalline cyclodextrin complex of the acid.[14] The i.r. spectra of the 1:1 complexes of HI with NH_3 or NMe_3 have been examined in four different matrix environments, Ar, O_2, N_2, C_2H_4, at 10K.[84] The symmetric I-H---N stretch was found to be markedly dependent on the nature of the matrix. A comparison with the spectra ofthe known XH-NH_3 and XH-NMe_3 adducts shows that the H-bond is stronger when X = I.

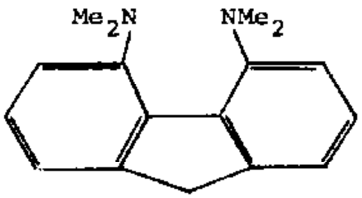
The H-bond energy of HF_2^- has been recalculated using a large flexible Gaussian basis set;[85] the value obtained, 169kJ mol^{-1}, agrees with a recent gas-phase ion cyclotron resonance determination of 163 kJ mol^{-1}. Similarly an improved value for the H-bond energy in $HOHF^-$ was obtained and the corresponding quantity calculated for $MeOHF^-$ for the first time. Crystal structure determinations of $MF(HF_2)$, M = Sr or Ba, have confirmed the interpretation of earlier n.m.r. studies, namely that the HF_2^- ions are asymmetric in these compounds.[86] ^{19}F n.m.r. studies of solutions of alkali metal fluorides in aliphatic diols and carboxylic acids have been reported.[87] Miller et al. concluded that the chemical shift data can be used only with caution as a very rough estimate of the strength of the interactions.

Truter[88a] has drawn attention to some errors arising from over-interpretation in the paper reported last year on the KF.malonic acid crystal structure.[88b] Emsley and coworkers[89] continue their study of H-bonding to F^- with a report on the crystal structure of CsF.succinic acid: here they identify chains of alternate succinic acid molecules and F^- ions linked through short H-bonds, $O-H---F^-$ = 2.449Å. Crystals of $KF.H_3PO_3$, mp. 170°C, as obtained from either the reaction of KF with H_3PO_3 or KH_2PO_3 with HF, are not identical with those crystallised from MeOH, and described as $(KHPO_3H.HF)_2$, mp. 96°C.[90] The H-bond energy of $HPO_3H_2F^-$ was calculated to be 61kJ mol^{-1}.

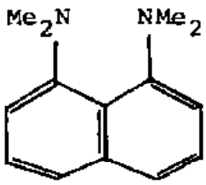
A new crystalline 1:1 complex of imidazole and trimethylphosphate has been prepared:[91] its i.r., ^1H and ^{15}N n.m.r. spectra reveal the presence of strong asymmetrical N-H---O=P bonds. Neutral and cationic transition metal amines interact with crown ethers in solution with N-H---O bond formation to give discrete or polymeric adducts, certain of which have been isolated in crystalline form.[92] Meot-Ner has investigated the interaction of polyethers and crown ethers with protons and with substituted ammonium ions in a pulsed high-pressure mass spectrometer.[93] The formation of H-bonds was inferred and proton affinities for a number of compounds were calculated.

From a study of the competitive decomposition processes of mixed ion clusters of the type $[(ROH)_n(H_2O)_m]H^+$, for $n+m < 20$, it has been possible to determine which component of a cluster preferentially solvates the proton.[94] For m = 1 an alcohol unit solvates the proton except for higher values of n. According to a survey of 900 organic crystal structures containing the group N-H---O=C the H-bond tends to occur along the directions of the O-sp^2 lone pairs, especially for shorter H---O distances.[95] However there are other influences, thus the geometries of intra- and inter-molecular H-bonds differ appreciably.

4,5-Bis(dimethylamino)fluorene (1) is reported to have a pK_a of



(1)



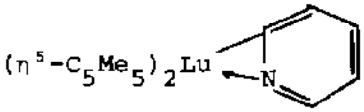
(2)

ca. 13.5, which implies greater basicity than that of 1,8-bis(dimethylamino)naphthalene (2), for which the term "proton sponge" has been used.[96]

7.2 HYDROGEN

Photosensitised H_2-evolution from basic aqueous silica colloids using N,N'-dipropyl-2,2'-bipyridiniumdisulphonate as electron acceptor and Pt as catalyst has been reported.[97] The quantum yield of H_2 at pH 8.5 was found to be 2.2 x 10^{-3}. The reduced clusters $[Mo_2Fe_6S_8(SPh)_9]^{n-}$, n = 3 or 4, and $[Fe_4S_4(SPh)_4]^{3-}$ cause H_2 to be generated from benzenethiol in pure DMF at ambient temperature.[98] Over a 24h period the yield of H_2 approached 100% for the n = 5 anion. The reaction kinetics were reported and possible mechanisms proposed. Cyclic voltammograms of buffered (pH 6.88) solutions of $[PtH(PEt_3)_3]^+$ at Hg electrodes show large reduction waves on all forward and reverse scans except the first.[99] Cole-Hamilton et al. interpret this in terms of catalytic H_2 production involving the adsorbed species $[PtH(PEt_3)_3]$, as monocation, radical and monoanion, and $[Pt(PEt_3)_3]$.

Facile H/D exchange has been achieved using $(\eta^5\text{-}C_5Me_5)_2LuMe$ by virtue of its ability to react with H_2(or D_2) forming $(\eta^5\text{-}C_5Me_5)_2LuH$ which can cleave C-H bonds, e.g. C_6H_6, or C-O bonds, e.g. Et-OEt.[100] Watson has also shown that the methyl and hydride compounds are even more active in the presence of suitable donors, e.g. OEt_2, when they react with py to form (3).



(3)

REFERENCES

1 N.Watanabe, J. Fluorine Chem., 22(1983)205.

2 V.Wray, Ann. Rept. on NMR Spectrosc., 14(1983)1.

3 W.L.Jolly and C.J.Eyermann, Inorg. Chem., 22(1983)1566.

4 K.O.Christe, J. Fluorine Chem., 22(1983)519.

5 T.V.Venkitachalam, P.Das and R.Bersohn, J. Am. Chem. Soc., 105(1983)7452.

6 M.J.Adam, J.M.Berry, L.D.Hall, B.D.Pate and T.J.Ruth, Can. J. Chem., 61(1983)658.

7 M.Diksic and Y.Toda, Can. J. Chem., 61(1983)661.

8 D.Naumann and H.Lange, J. Fluorine Chem., 23(1983)37.

9 D.M.Jewett and R.E.Ehrenkaufer, J. Fluorine Chem., 22(1983)475.

10 T.Mallouk and N.Bartlett, J. Chem. Soc., Chem. Commun., (1983)103.

11 I.Palchan, D.Davidov and H.Selig, J.Chem. Soc., Chem. Commun., (1983)657.

12 K.B.Nielsen, B.Toft, K.C.Mishra, S.K.Mishra, K.J.Duff and T.P.Das, J. Am. Chem. Soc., 105(1983)1734.

13 O.Waernes, F.Palmisano and T.Østvold, Acta Chem. Scand., Ser. A, 37(1983)207; O.Waernes and T.Østvold, Acta Chem. Scand., Ser. A, 37(1983)293.

14 Y.Tanaka, H.Sakuraba and H.Nakanishi, J. Chem. Soc., Chem. Commun., (1983)947.

15 D.M.Storch, C.J.Dymek and L.P.Davis, J. Am. Chem. Soc., 105(1983)1765.

16 D.J.Bristow and G.M.Bancroft, J. Am. Chem. Soc., 105(1983)5634.

17 J.P.Yesinowski and M.J.Mobley, J. Am. Chem. Soc., 105(1983)6191.

18 K.Garber and B.S.Ault, Inorg. Chem., 22(1983)2509.

19 M.Attiná, F.Cacace and A.P.Wolf, J. Chem. Soc., Chem. Commun., (1983)108.

20 S.Dermiek and Y.Sasson, J. Fluorine Chem., 22(1983)431.

21 S.J.Brown and J.H.Clark, J. Chem. Soc., Chem. Commun., (1983)1256.

22 D.Fenske, R.Kujanek and K.Dehnicke, Z. Anorg. Allg. Chem., 507(1983)51.

23 R.H.Crabtree, G.G.Hlatky and E.M.Holt, J. Am. Chem. Soc., 105(1983)7302.

24 J.W.Larson and T.B.McMahon, J. Am. Chem. Soc., 105(1983)2944.

25 B.S.Ault, Inorg. Chem., 22(1983)2221.

26 J.-P.Kintzinger, J.-M.Lehn, E.Kauffmann, J.L.Dye and A.I.Popov, J. Am. Chem. Soc., 105(1983)7549.

27 S.Pohl, Z. Anorg. Allg. Chem., 498(1983)15,20.

28 R.J.H.Clark, M.Kurmoo, A.M.R.Galas and M.B.Hursthouse, J. Chem. Soc., Dalton Trans., (1983)1583.

29 L.R.Gray, D.J.Gulliver, W.Levason and M.Webster, Inorg. Chem., 22(1983)2362.

30 R.Dreyer, I.Dreyer, F.Rösch and S.Fischer, Z. Chem., 23(1983)346.

31a A.S.Batsanov, Yu.T.Struchkov and S.A.Batsanov, Dokl. Akad. Nauk SSSR., 251(1980)251,347.

31b H.G. von Schnering and D.Vu, Angew. Chem., Int. Ed. Engl., 22(1983)408.

32 Y.Apeloig, B.Gommer, G.Frenking, M.Karni, A.Mandelbaum, H.Schwarz and A.Weisz, J. Am. Chem. Soc., 105(1983)2186.

33 R.L.DeKock, C.P.Jasperse, D.T.Dao, J.H.Breda and J.F.Liebman, J. Fluorine Chem., 22(1983)575.

34 V.V.Bardin, G.G.Furin and G.G.Yakobson, J. Fluorine Chem., 23(1983)67.

35 V.A.Vopilov, V.M.Buznik, V.F.Sukhoverkhov and A.V.Sharabarin, Russ. J. Inorg. Chem., 28(1983)350.

36 F.G.Il'in, V.F.Sukhoverkhov, A.V.Sharabarin and Yu.A.Buslaev, Dokl. Akad. Nauk SSSR., 271(1983)652.

37 K.O.Christe and W.W.Wilson, Inorg. Chem., 22(1983)1950.

38 K.O.Christe, W.W.Wilson and E.C.Curtis, Inorg. Chem., 22(1983)3056.

39 L.K.Blair, K.D.Parris, P.S.Hii and C.P.Brock, J. Am. Chem. Soc., 105(1983)3649.

40 S.Karunanithy and F.Aubke, Can. J. Chem., 61(1983)2638.

41 K.O.Christe, W.W.Wilson, R.D.Wilson, R.Bougon and T.B.Huy, J. Fluorine Chem., 23(1983)399.

42 R.J.Gillespie, R.Kapoor, R.Faggiani, C.J.L.Lock, M.Murchie and J.Passmore, J. Chem. Soc., Chem. Commun., (1983)8.

43 K.-F.Tebbe, Acta Crystallogr., C39(1983)154.

44 A.J.Jircitano and K.B.Mertes, Inorg. Chem., 22(1983)1828.

45 G.M.Anderson, I.F.Fraser and J.M.Winfield, J. Fluorine Chem., 23(1983)403.

46 S.Sundstrand, Acta Chem. Scand., Ser. A, 37(1983)777, 787.

47 T.Birchall and R.D.Myers, Inorg. Chem., 22(1983)1751.

48 W.C.Child and G.N.Papatheodorou, J. Phys. Chem., 87(1983)271.

49 H.Dörner, K.Dehnicke, W.Massa and R.Schmidt, Z. Naturforsch., Teil B, 38(1983)437.

50 K.-F.Tebbe and R.Fröhlich, Z. Anorg. Allg. Chem., 505(1983)7, 19.

51 V.N.Petrov, S.V.Lindeman, Yu.T.Struchkov, F.A.Chugtai, V.A.Budylin and Yu.G.Bundel, Dokl. Chem., 269(1983)113.

52 M.Papadopoulou and A.Varvoglis, J. Chem. Res. (S), (1983)66.

53 T.P.Lockhart, J. Am. Chem. Soc., 105(1983)1940.

54 M.Cartwright and A.A.Woolf, Polyhedron, 2(1983)811.

55 L.Hadjiarapoglou, S.Spyroudis and A.Varvoglis, J. Chem. Res. (S), (1983)50.

56 T.Birchall and R.D.Myers, J. Chem. Soc., Dalton Trans., (1983)885.

57 H.J.Frohn, G.Holtus and W.Pahlmann, J. Fluorine Chem., 23(1983)445.

58 J.M.Shreeve, Adv. Inorg. Chem. Radiochem., 26(1983)119.

59 C.J.Schack, W.W.Wilson and K.O.Christe, Inorg. Chem., 22(1983)18.

60 W.Maya, D.Pilipovich, M.G.Warner, R.D.Wilson and K.O.Christe, Inorg. Chem., 22(1983)810.

61 F.Temps, H.Gg.Wagner, P.B.Davies, D.P.Stern and K.O.Christe, J. Phys. Chem., 87(1983)5068.

62 M.E.Jacox, J. Phys. Chem., 87(1983)4940.

63 S.Stavber and M.Zupan, J. Chem. Soc., Chem. Commun., (1983)563.

64 V.C.Hand and D.W.Margerum, Inorg. Chem., 22(1983)1449.

65 S.C.Bhatia, M.George-Taylor, C.W.Merideth and J.H.Hall, J. Phys. Chem., 87(1983)1091, 3362.

66 H.E.Fonouni, S.Krishnan, D.G.Kuhn and G.A.Hamilton, J. Am. Chem. Soc., 105(1983)7672.

67 B.C.Schardt and C.L.Hill, Inorg. Chem., 22(1983)1563.

68 W.J.Masschelein, in 'Chlorine Dioxide', ed. R.G.Rice, Ann Arbor Science Publ., Ann Arbor, Michigan, (1979).

69 R.C.Loupec and J.Potier, J. Chem. Phys., 80(1983)449.

70 I.R.Beattie and J.E.Parkinson, J. Chem. Soc., Dalton Trans., (1983)1185.

71 L.Stein and E.H.Appelman, Inorg. Chem., 22(1983)3017.

72 K.M.Barkigia, L.D.Spaulding and J.Fajer, Inorg. Chem., 22(1983)349.

73 A.A.Vigalok, G.G.Petrova, S.G.Lukashina and I.V.Vigalok, Russ. J. Inorg. Chem., 27(1982)1091.

74 J.H.Holloway, D.Laycock, G.A.Schumacher, T.R.G.Syvret and G.I.Schrobilgen, J. Fluorine Chem., 23(1983)443, 444.

75 G.L.Johnson and L.Andrews, J. Am. Chem. Soc., 105(1983)163.

76 G.L.Johnson and L.Andrews, J. Phys. Chem., 87(1983)1852.

77 M.E.Friedlander, J.M.Howell and A.-M.Sapse, Inorg. Chem., 22(1983)100.

78 D.Hass, E.Kemnitz and M.Rönnebeck, Z. Chem., 23(1983)142, 232, 312.

79 K.S.Mohamed, D.K.Padma, R.G.Kalbandkeri and A.R.V.Murthy, J. Fluorine Chem., 23(1983)509.

80 D.Devilliers, F.Lantelme and M.Chimia, J. Chim. Phys., 80(1983)267.

81 G.A.Bottomley, J.B.Farrow and F.J.Lincoln, Aust. J. Chem., 36(1983)649.

82 J.Carre and G.Perachon, J. Fluorine Chem., 23(1983)309; J.Thourey, S.Bendaoud and G.Perachon, J. Fluorine Chem., 23(1983)331.

83 J.Thourey, P.Germain and G.Perchon, J. Fluorine Chem., 22(1983)505.

84 L.Schriver, A.Schriver and J.P.Perchard, J. Am. Chem. Soc., 105(1983)3843.

85 J.Emsley, R.J.Parker and R.E.Overill, J. Chem. Soc., Faraday Trans. 2, 79(1983)1347.

86 W.Massa and E.Herdtweck, Acta Crystallogr., C39(1983)504.

87 J.M.Miller, R.K.Kanippayoor and J.H.Clark, J. Chem. Soc., Dalton Trans., (1983)683.

88a M.R.Truter, J. Chem. Soc., Dalton Trans., (1983)187.

88b J.Emsley, D.J.Jones and R.Kuroda, J. Chem. Soc., Dalton Trans., (1982)1179.

89 J.Emsley, D.J.Jones and R.Kuroda, Acta Crystallogr., C39(1983)729.

90 J.Emsley, J.Lucas, R.J.Parker and R.E.Overill, Polyhedron, 2(1983)19.

91 J.H.Clark, M.Green and R.G.Madden, J. Chem. Soc., Chem. Commun., (1983)136.

92 H.M.Colquhoun, D.F.Lewis, J.F.Stoddart and D.J.Williams, J. Chem. Soc., Dalton Trans., (1983)607.

93 M.Meot-Ner, J. Am. Chem. Soc., 105(1983)4906, 4912.

94 A.J.Stace and C.Moore, J. Am. Chem. Soc., 105(1983)1814.

95 R.Taylor, O.Kennard and W.Versichel, J. Am. Chem. Soc., 105(1983)5761.

96 H.A.Staab, T.Saupe and C.Krieger, Angew. Chem., Int. Ed. Engl., 22(1983)731.

97 Y.Degani and I.Willner, J. Chem. Soc., Chem.,Commun., (1983) 710.

98 T.Yamamura, G.Christou and R.H.Holm, Inorg. Chem., 22(1983)939.

99 J.R.Fisher, R.G.Compton and D.J.Cole-Hamilton, J. Chem. Soc., Chem. Commun., (1983)555.

100 P.L.Watson, J. Chem. Soc., Chem. Commun., (1983)276.