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Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 THE HALOGENS

7.1.1 The Elements

A number of reviews have appeared in the literature to commemorate the discovery of fluorine in 1886 by Moissan, with a whole issue of the the Journal of Fluorine Chemistry [1] devoted to celebrating this discovery. The history of fluorine chemistry is comprehensively covered here, along with reviews of many aspects of modern fluorine chemistry. The abstracts of papers given at the International Symposium held in August 1986 to mark the centenary of Moissan's discovery have been recorded in another issue of the Journal of Fluorine Chemistry.[2] Finally, a book entitled "Fluorine - The First Hundred Years (1886-1986)" has been published to celebrate this event.[3] The work of the fluorine and HF pioneer, J.H.Simons, has been commemorated by a review of his work [4] and a reprint of his address [5] on receiving the award for "Creative Work in Fluorine Chemistry" in July 1973. W.H.Pearlson [6] has also given a description of Simon's Electrochemical Fluorination process.

The dynamics of fluorescence decay of halogens and interhalogens have been reviewed by Heaven.[7] Also reported are the proceedings of the International Symposium on Radiohalogens held in Canada in September 1985.[8]

Although there have been reports tha F_2 gas is in fact colourless, a reexamination [9] has confirmed Moissan's original observation that the gas is yellow in colour. Liquid fluorine is coloured, described in this publication as being "canary yellow".

A novel displacement reaction described by Christe [10] leads to formation of elemental fluorine, equation (1). The novelty

$$K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + MnF_3 + {}^1/_2F_2 \qquad \ldots(1)$$

of the preparation lies in the fact that both starting materials do not require F_2 for their preparations.

Various olefins are epoxidised by making use of the $F_2/H_2O/MeCN$ system which behaves as an oxidising rather than a fluorinating reagent.[11] The epoxidation is stereoselective, with yields in excess of 80% . A crucial step is believed to be the formation of hypofluorous acid, HOF, which then reacts with the acetonitrile. Both MeCN and H_2O are needed for epoxidation to take place, a result confirmed by reactions using pure, dry MeCN which was found to be non-fluorinating.

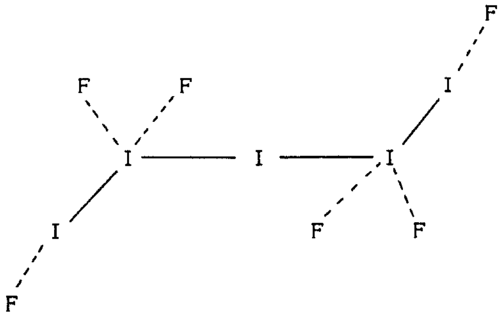
Matrix isolation techniques have been employed for the reactions of halogens with various compounds at low temperatures.[12-14] The reaction of Cl_2 with Me_2S in an argon matrix gives a series of 1:1 addition complexes which have been analysed by infra-red spectroscopy.[12] Infra-red spectroscopy has also been used in determining the nature of the complex formed when ozone and bromine are condensed together in an argon matrix.[13] Subsequent photolysis of the weak $O_3...Br_2$ complex gave a series of new species, one of which contained the bridging Br-O-Br unit.

A series of 1:1 complexes has also been formed when cyclopropane or its derivatives are codeposited with Cl_2, Br_2, or ClF in an argon matrix.[14] In each case, interactions occur at the midpoint of the C-C bond, a result obtained by investigations using far-infrared spectroscopy. A wide variety of products has been obtained by the room temperature gas phase photolysis of mixtures of Cl_2 and various nitriles.[15] For example, with CF_3CN, the three products observed are $CF_3CCl{=}NCl$, $CF_3CCl{=}N{-}N{=}CClCF_3$ and CF_3CCl_3, whilst when the nitrile used in HCN, the photolysis products are ClCN, $CCl_2{=}NCl$ and CCl_4. Pulsed radiolysis of an aqueous solution of NaCl has given the reactive Cl_2^- radical as a reaction product.[16] This radical oxidises various actinide ions including U(V), Np(V), Pu(V) and Am(III).

The reaction of iodine with various MF_6 species (M = Mo,U) in MeCN at ambient temperatures has yielded ionic solvates of the general formula $[I(NCMe)_2]MF_6$.[17] The vibrational spectra of the compounds imply linear coordination of MeCN to I^+. On standing in MeCN, decomposition is said to occur to I_2.

The kinetics of the hydrolysis of I_2 to HOI and I^- have been studied by temperature-jump spectrophotometry.[18] The results conclude that the rate of hydrolysis is dependent on the rate of disproportionation of the conjugate base I_2OH^-. This is contrary to the results previously obtained for the hydrolysis of Cl_2 and Br_2.

The planar, centrosymmetric $[AsF_6][I_5]$ ion pair has been isolated by oxidation of I_2 by AsF_5 in liquid SO_2.[19] The structure of the I_5^+ cation, showing cation/anion interactions is shown in (1).



(1)

7.1.2 Halides

The use of a fluoride ion selective electrode for the determination of the fluoride content in various matrices of environmental and geochemical interest has been discussed by Sayer.[20] A high resolution solid state ^{19}F n.m.r. investigation into the bonding in ionic fluorides has been reported by Clark et al.[21] The compounds studied include the alkali metal fluorides along with Et_4NF and Bu_4NF. They conclude that the F^- ion exhibits a much wider range of chemical shift values in the solid state than in solution. This was said to be due to the presence of ion pairing and the coordinative unsaturation of F^- in the solid state.

Two research groups [22,23] have reported the enhancement or the reactivity of MF (M = K,Cs) as a fluorinating agent by addition of CaF_2 either in combination with the metal fluoride or as a support reagent. The $MF-CaF_2$ support reagent is most effective in the fluorination of various organic chlorides and bromides under mild conditions.[23] The results for the fluorination of benzyl bromide in MeCN at 80°C using various forms of the CsF/CaF_2 fluorinating agent are shown in Figure 1.

A study [24] into the phase catalysed exchange reaction between alkali metal halides and alkyl halides, equation (2), has shown that the equilibrium position strongly depends on the nature of M and the amount of water present in the reaction mixture.

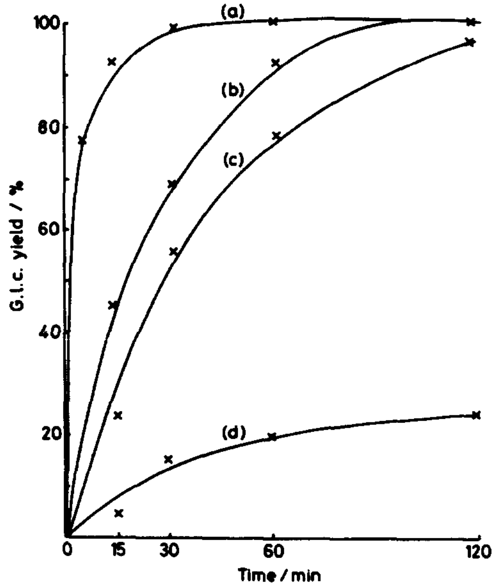


Figure 1. Rate of production of $PhCH_2Br$ in MeCN at 80°C using (a)$CsF-CaF_2$ (dried at 80°C/reduced pressure); (b) CsF (dried at 80°C/reduced pressure); (c) CsF with added CaF_2 (untreated); and (d) CsF (untreated); (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)791).

$$RCl + MBr \rightleftharpoons RBr + MCl \qquad ...(2)$$

R = primary alkyl group, M = Li,Na,K or Cs.

The first high resolution ^{19}F n.m.r. spectrum has been recorded for 1,2-difluoroethane.[25] The results give the conformational energy difference between the gauche and trans forms to be approximately -0.8 kcal.mol^{-1}. This information was obtained from analysis of the coupling constants recorded in both the ^{19}F and ^{1}H n.m.r. spectra.

The synthesis of new mono-organothallium(III) derivatives have proved useful for the chlorination of various aliphatic ketones.[26] The two stage reaction involves the use of $TlCl_3$

firstly to prepare the organothallium(III) derivative (equation 3), and subsequently to react with this derivative to produce the chlorinated aliphatic ketone (equation (4). The course of

$$\underset{}{TlCl_3 + MeC(:O)CH_2R \longrightarrow \underset{(A)}{Cl_2TlCH_2C(:O)CH_2R} + HCl} \qquad ...(3)$$

$$(A) + {}^1/_3TlCl_3 \longrightarrow MeC(:O)CHClR + {}^1/_3Tl_3[TlCl_6] \qquad ...(4)$$

R = alkyl.

both reactions was monitored by ^{1}H, ^{13}C and ^{250}Tl n.m.r. spectra.

A novel lithium/chlorine cationic species (Figure 2) with a

$$pmdeta + [Li(thf)_4][Li\{C(SiMe_3)_3\}_2] + LiCl$$

$$[(pmdeta)Li(\mu\text{-}Cl)Li(pmdeta)][Li\{C(SiMe_3)_3\}_2] \qquad ...(5)$$

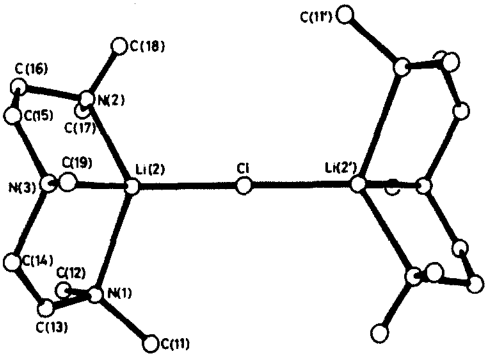
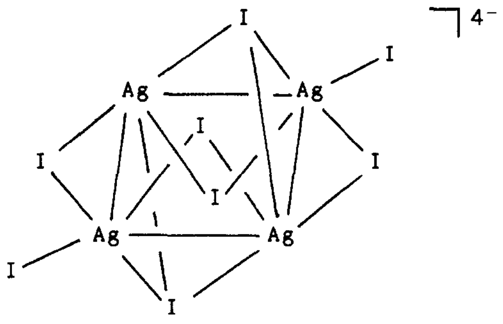


Figure 2. Structure of the $[Li_2(pmdeta)_2Cl]^+$ cation (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)969).

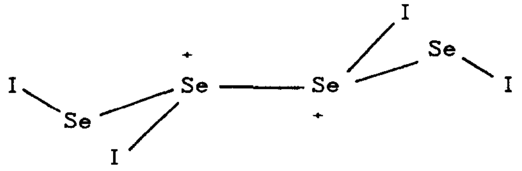
central linear Li-Cl-Li system has been isolated from a reaction in toluene between $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$ (pmdeta) and $[Li(thf)_4][\{C(SiMe_3)_3\}_2]$ containing some LiCl equation (5).[27]

A novel silver iodide anion, $[Ag_4I_8]^{4-}$ has been identified the bis(6,9-diazoniadispiro[5.2.5.3]heptadectone salt.[28] The anion (2) contains two triply bridging and four doubly bridging iodine ions.

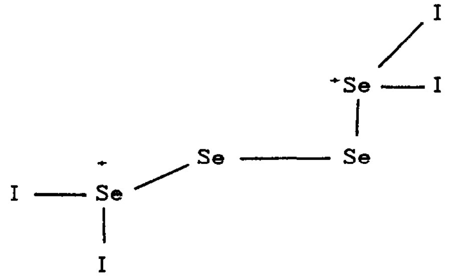


(2)

The $[Se_4I_4]^{2+}$ cation formed by the reaction of $Se_4(AsF_6)_2$ and I_2 in liquid SO_2 has been characterised in solution by ^{77}Se



(3)



(4)

n.m.r.[29] The two possible structures proposed for the cation are shown in (3) and (4).

The largest iodocuprate ion so far observed has been found in the crystal structure of $(PyH)_2(Cu_3I_5)$ which is more correctly formulated as $(pyH)_{24}([Cu_3I_{56}]I_4)$.[30] The CuI_4 tetrahedra present in this structure are linked through 2 or 3 common edges to form the symmetrical polyanion $[Cu_{36}I_{56}]^{20-}$ with very rare symmetry 432 (O). A series of new types of uranium tetraiodides has been prepared by du Preez et al.[31] The starting materials were obtained from the elements and diphenyl ketone (equation 6); the coordinated diphenylketone can be exchanged for MeCN (equation 7). Either of the products may be used as shown in equation (8) to obtain the neu complexes.

$$U + 4I_2 + 2dpk \xrightarrow{CH_2Cl_2/N_2\ atm} UI_4(dpk)_2 \qquad ...(6)$$

$$UI_4(dpk)_2 \xrightarrow{MeCN/-18°C} UI_4(MeCN)_4 + 2dpk \qquad ...(7)$$

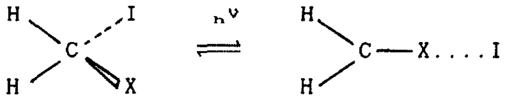
$$UI_4(dpk)_2 \text{ or } UI_4(MeCN)_4 \xrightarrow{2L/MeCN} UI_4L_{2(s)} \qquad ...(8)$$

L = L,N,N',N'-tetramethylurea or Ph_3PO.

7.1.3 Interhalogens and Related Species

The partial structure of the interhalogen OCN-Br has been determined by microwave spectroscopy.[32] The molecule is planar with a Br-N separation of 185pm.

Matrix isolation in argon shows the presence of new photoisomers of several dihalomethanes.[33] Photolysis brings about migration of iodine from carbon to halogen (equation 9),



...(9)

(5)

X = I(a), Br(b) or Cl(c)

with the product formulated as a resonance hybrid between unsolvated contact ion pairs (equation 10). Isomers (5a [violet]), (5b [green]) and (5c [yellow]) can be converted into the educts by changing the frequency of irradiation.

$$\overset{+}{H_2C}-X\cdots\overset{-}{I} \longleftrightarrow H_2C=\overset{+}{X}\cdots\overset{-}{I} \qquad \ldots(10)$$

(<u>5c</u>)

Matrix isolation techniques have also been used in a study into the stability of the sulphurones SCl_3F, SCl_2F and $SClF_3$, formed in the gas phase by co-condensation of SCl_2 with ClF and F_2.[34] The most stable species is SCl_2F_2 to which C_{2v} symmetry is assigned.

Sudden mixing of ClF_3 with various halocarbons at temperatures of 25°C downwards results in an explosive reaction, the mechanism for which is said to be ionic, with all reactions initiating within 1ms of contact between the reactants.[35] Thg calculated electronic charge distribution of the ClF_6^- anion confirms the view that AX_6E systems should distort from octahedral symmetry in the gas phase, due to the presence of a stereochemically active lone pair.[36]

When Br_2 and F_2 are reacted together at -75°C, the interhalogen BrF is produced, which has then been used as a novel aromatic brominating agent for various activated and non-activated aromatic ring systems.[37] For example, reaction with toluene gives 50/50 para:ortho bromination. However, reaction with the less ring activated phenyl acetate, gives 100% para bromination. All rections are complete within 15 minutes.

Reaction of BrF_5 with $C_6F_5SiF_3$ in a weakly basic aprotic medium gives $C_6F_5BrF_4$ as a volatile colourless solid melting at 88°C.[38] The chemical and spectroscopic properties of this compound differ from those reported earlier, with for example, base hydrolysis at pH>10 following equation (11). Reaction with R_3P gives C_6F_5Br and R_3PF_2 and with Me_3SiCl the products are shown in equation (12).

$$C_6F_5BrF_4 + 5OH^- \longrightarrow C_6F_5H + BrO_3^- + 4F^- + 2H_2O \qquad \ldots(11)$$

$$C_6F_5BrF_4 + 4Me_3SiCl \longrightarrow C_6F_5Br + 4Me_3SiF + 2Cl_2 \qquad \ldots(12)$$

Low temperature metathesis reactions, equations (13) and (14), are synthetic routes to both the ionic species $NF_4^+BrF_4^-$ and $NF_4^+BrF_4O^-$.[39] Both compounds are unstable, with NF_4BrF_4O

$$NF_4SbF_6 + CsBrF_4 \xrightarrow{BeF_5/-31^{\circ}C} CsSbF_6 + NF_4BrF_4 \qquad ...(13)$$

$$NF_4SbF_6 + CsBrF_4O \xrightarrow{BrF_5/-55^{\circ}C} CsSbF_6 + NF_4BrF_4 \qquad ...(14)$$

producing a small amount of NF_3 even at -55°C, equation (15). NF_4BrF_4 is more stable but also decomposes, but to different products, equation (16).

$$NF_4BrF_4O \longrightarrow NF_3 + F_2 + BrF_3O \qquad ...(15)$$

$$NF_4BrF_4 \longrightarrow NF_3 + BrF_5 \qquad ...(16)$$

The first completely symmetrical Br_3^- anion has been identified in the compound $[VBr_2(MeCN)_4]Br_3$. From an X-ray study, the anion is rigorously linear with Br-Br distances of 254.8pm.[40]

Reactions of chlorine with mixtures of I_2 and PCl_5 in either CH_2Cl_2 or $POCl_3$ as solvent leads to crystals of the tetrachloroiodate, $[PCl_4][ICl_4]$.[41] An X-ray structure shows the expected tetrahedral cation and square planar anion, but of the two crystallographically independent anions, one has almost ideal D_{4h} symmetry, whilst the second is distorted with C_{2v} symmetry. The I-Cl distances range between 246.1 and 250.8pm. There are however short I...Cl intermolecular contacts at 354 and 370pm which are usually in the same direction as the non-bonding pair of electrons on the central iodine atom. These secondary bonds raise the coordination number of one iodine to six, whilst the other remains at four.

A novel transformation of CO and isoelectronic groups to the CF_2 group has been accomplished by the in situ synthesis of IF.[42] The F^- ion in this interhalogen is highly nucleophilic as it is not heavily solvated, which is the case in most other sources. Hence IF may be reacted with various hydrazone derivatives under very mild conditions. An example of the transformation to CF_2 is shown in equation (17).

$$PhC(=NNH_2)R + 2IF \longrightarrow PhCF_2R + NH_2NI_2 \qquad ...(17)$$

R = Ph, or Me.

A sequential reaction between I_2Cl_6 and $AgNO_3$ (equation 18) has been observed by Derakshan et al.[43]

$$3I_2Cl_6 + 24AgNO_3 + 12H_2O \longrightarrow 18AgCl + 2AgI + 4AgIO_3 + 24HNO_3 \quad ...(18)$$

X-ray analyses for RbI_3 and TlI_3 show them to be isotypes of the CsI_3 structure.[44] The I_3^- ions are asymmetric with I-I distances ranging between 283.3 and 305.1pm. The I_3^- ion is also slightly bent (178.1°) in the Rb compound. The asymmetry of the anions is discussed in terms of cationic size.

The structures of various ionic polyiodides have been partially obtained from studies of their vibrational spectra.[45] The compounds Me_4NI_5 and $(TMA.H_2O)_{10}HI_5$ both contain the I_5^- unit. In the former, the I_5^- ion is bent, whilst in the latter it is linear. Both $(Phen)_2HI_5$ and Et_4NI_7 contain the I_3^- anion with one and two molecules of I_2 respectively, whilst Me_4NI_9 can be described as $(I_5^-)(2I_2$.

IF_5 is a versatile oxidising agent for organo Group 5 compounds.[46,47] Oxidation of alkyl and aryl phosphines, such as R_3P, R_2PF, R_2PCl and $RPCl_2$, to the corresponding fluorophosphoranes occurs in a one step process at or below 0°C. The only by-product observed was elemental I_2; neither IF_3 nor IF was detected.[46] Although trialkylarsines and stibines could be oxidised similarly to the corresponding arsoranes and stiboranes in good yields, bismuthines gave different products depending on the type of organic group present.[47] For example, oxidation gave either R_3BiF_2, or fluorobismuthines, formed by RF elimination from unstable difluorobismuthoranes. Oxidation of substituted arsenic and stibinic chlorides, R_nMCl_{3-n} ($n = 1,2$), with IF_5 generally led to the corresponding tri- and tetrafluorides.

7.1.4 Oxides, Oxide Halides and Oxoanions

A reconsideration of the infra red and Raman spectra or solid HOF and HNF_2 has indicated that the structures of the compounds are best interpreted in terms of hydrogen-bridged aggregates involving nitrogen and oxygen, rather than fluorine, as the hydrogen acceptor.[48] This is considered to be more reasonable as the hydrogen atoms in each moleculae are attached to oxygen and nitrogen, thus releasing electrons to the fluorine ligands. The most negative charge resides on oxygen and nitrogen, making the OH and NH groups more basic than fluorine.

The passage of F_2 over ice at -50°C gives mixtures of O_2, HOF, OF_2 and traces of H_2O_2.[49] The role of HOF in producing the OF_2 was established using ^{18}O and ^{19}F labelling. The results showed that OF_2 contains one F atom from HOF and one from F_2 (equation 19).

$$F_2 + HOF \longrightarrow OF_2 + HF \qquad ...(19)$$

The structure of a fluoride adduct of oxalyl fluorides, i.e. the $C_2F_3O_2^-$ anion, has been investigated by infra red matrix isolation spectroscopy.[50] Both the cis and the trans forms were produced by reacting CsF with $C_2F_2O_2$ in the matrix. The occurrence of (C-O) and (C-F) stretching frequencies at 1450-1500 and 900cm^{-1} respectively, coupled with the presence of low frequency vibrational modes at ~400cm^{-1} lend support to a fluorine bridged structure. Warming to room temperature gave a $CsCF_3CO_2$ deposit on the cell windows, implying that the bridged form of the anion is unstable and rearrangement takes place to give the more stable $CF_3CO_2^-$ form.

Hartree Fock MP4SDTQ level m.o. calculations for HOCl and its valence isomer HClO show that the activation energy for interconversion is 74±5 kcal.mol^{-1} and that the latter lies some 67 kcal.mol^{-1} above the ground state of HOCl.[51] The molecular structure of HOCl has also been determined by microwave spectroscopy.[52] The reaction of O_3, Cl_2O or O_2Cl with chlorine atoms in a flow system at 220-240K yields Cl_2O_2.[53] The product exists as two dimeric isomers, namely ClOOCl and the less abundant ClOClO. The kinetics of the reaction of Cl(III) with bromine (equation 20) have been studied by stopped flow spectrophotometry.[54] The rate determining step was found

$$2HClO_2 + Br_2 \longrightarrow 2ClO_2 + 2Br^- + 2H^+ \qquad ...(20)$$

to be the subsequent reaction with $BrClO_2$, equation (21).

$$BrClO_2 + HClO_2 \longrightarrow 2ClO_2 + Br^- + H^+ \qquad ...(21)$$

At pH 7.41, bromine was present as BrOH. A comparison of rate constants for the ClO_2H/Br_2 and $BrOH/ClO_2H$ reactions showed that

BrOH was less reactive than Br_2 towards Cl(III). Similar work carried out by the same authors [55] on the Cl(III)/Br^- system showed two results. Firstly, with excess Br^-, both Br_3^- and Cl^- were produced (equation 22). Secondly, with excess Cl(III),

$$HClO_2 + 6Br^- + 3H^+ \longrightarrow 2Br_3 + Cl^- + 2H_2O \qquad ...(22)$$

both ClO_2 and Br_2 were produced, which gave rise to a complex sixteen step reaction mechanism.

Tobias and Jansen[56] have determined the crystal structure of Cl_2O_6 at low temperature. In the solid state, Cl_2O_6 exists as an ionic chloryl perchlorate, $ClO_2^+ClO_4^-$, with a Cl-O distance in the cation of 141pm, which is considerably shorter than that found in ClO_2 gas (147.5pm). Each cation is coupled with two anions and vice versa, to give the polymeric structure shown in Figure 3.

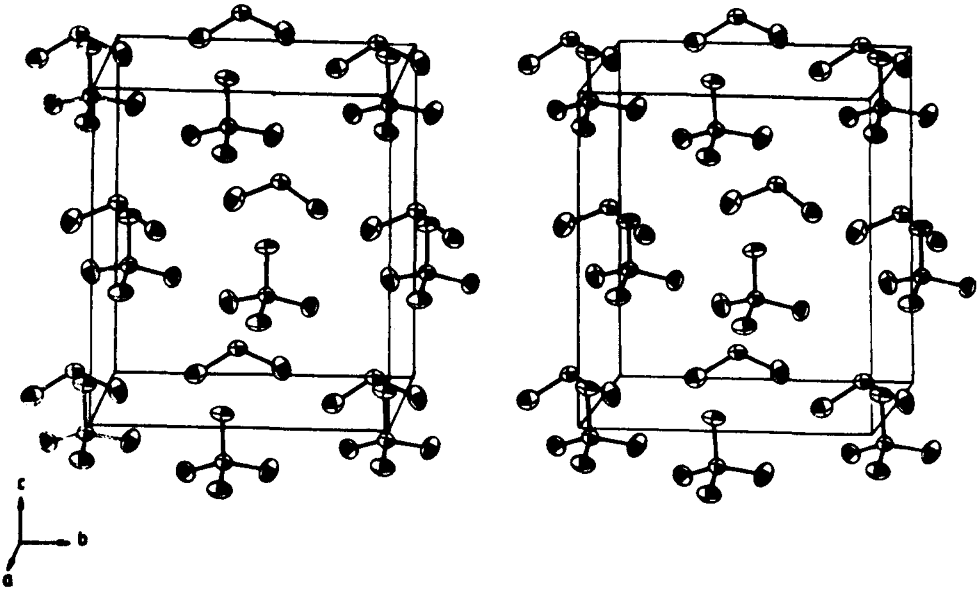


Figure 3. Stereoview of Cl_2O_6 (reproduced by permission from Angew. Chem., Int. Ed. Engl., 25(1986)993).

Reaction of Cl_2O_6 with $TiCl_4$ at -180°C gives the solvate $Ti(ClO_4)_4.xCl_2O_6$, with unsolvated $Ti(ClO_4)_4$ obtained by vacuum sublimation at 42-45°C.[57] Single crystal structural analysis shows that the $Ti(ClO_4)_4$ units are independent of each other, with the titanium atoms chelated by four ClO_4^- ligands. The average Ti-O distance is 206.9pm. The overall symmetry of the molecule is C_2 with the ClO_4^- units distorted by the presence of bonded and free oxygen atoms. The vibrational spectra are fully consistent with the X-ray data. The reaction between ClO_4^- and M(III) species (M = Nd, Tb, Eu and Er) in MeCN has been studied by vibrational spectroscopy.[58] In solution, vibrations due to unidentate, bidentate and undissociated ClO_4^- are seen, although the amount of bidentate coordination is low.

Three new N-perchloryl compounds (equations 23-25) have been obtained when azetidine, aziridine and adamantylamine were treated with Cl_2O_7.[59] In addition, the K^+, Na^+, Me_4N^+ and

$$2C_3H_6NH + Cl_2O_7 \longrightarrow C_3H_6NH_2[ClO_4] + C_3H_6NClO_3 \qquad ...(23)$$

$$2C_2H_4NH + Cl_2O_7 \longrightarrow C_2H_4NH_2[ClO_4] + C_2H_4NClO_3 \qquad ...(24)$$

$$2C_{10}H_{15}NH_2 + Cl_2O_7 \longrightarrow C_{10}H_{15}NH_3[ClO_4] + C_{10}H_{15}NHClO_3 \qquad ...(25)$$

Ba^{2+} salts of the adamantyl product were also isolated.

Hydrates of several halate species, namely $Sr(BrO_3)_2.H_2O$, $Ba(BrO_3)_2.H_2O$, $Ba(IO_3)_2.H_2O$, $Pb(ClO_3)_2.H_2O$ and $Pb(BrO_3)_2.H_2O$ are isostructural and single crystal data have been obtained for all compounds.[60] The mean distances and angles are shown in Table 1. Hydrogen bonding leads to O...O separations varying from 273.6pm in $Pb(BrO_3)_2.H_2O$, to 289.1pm in $Ba(ClO_3)_2.H_2O$.

Table 1. Mean bond distances (pm) and angles (°) for $M(XO_3)_2.H_2O$ (M = Sr, X = Br; M = Ba, X = Br,I; M = Pb, X = Cl,Br).

X-O(pm)		O-X-O(°)	
	Distance		Angle
Cl-O	149.0	O-Cl-O	106.4
Br-O	165.9	O-Br-O	104.0
I-O	180.2	O-I-O	99.6

The proposed mechanism[61] for the reaction between BrO_3^- and

I^- in aqueous acid involves the formation of IBr and the overall reaction scheme is summarised in equations (26) to (29):

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow 3I_2 + Br^- + 3H_2O \qquad ...(26)$$

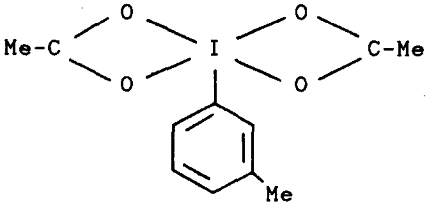
$$I_2 + BrO_3^- \longrightarrow IBr + IO_3^- \qquad ...(27)$$

$$IBr + BrO_3^- \longrightarrow Br_2 + IO_3^- \qquad ...(28)$$

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + H_2O \qquad ...(29)$$

The complete reaction mechanism involves thirteen elementary steps, none of which involves radical species.

The structure of m-tolyl iodine diacetate (6) shows T-shaped coordination about I(III) from the carbon of the phenyl ring and two oxygens from the acetate group with an average I-O bond length of 213.7pm.[62] Coordination is completed by two further I...O intermolecular contacts of average length 286pm.



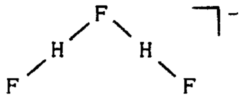
(6)

7.1.5 Hydrogen Halides

Ab initio calculations on F_2H^+ and the topological FHF^+ form have shown that the most stable form is the protonated F_2 species.[63] The $H\dot{X}^-$ radical anions are formed when Me_3NSO_3 doped with Me_3NHX (X = F,Cl,Br and I) is irradiated with ^{60}Co γ-radiation at 77K.[64] When X = Cl, Br or I, radical anions were formed with semi-occupied δ^* m.o's. The HF^- radical, however, showed the properties of normal trapped H-atoms.

N-fluoroisopropyl carbamate, $Pr^iOC(:O)NHF$, reacts with HF at room temperature to form a new monofluoroammonium salt $NH_3F^+HF_2^-.nHF$.[65] Reactions with AsF_5, SbF_5 and BF_3 lead to the salts of the corresponding fluoroanions.

Mootz et al. have isolated several poly(hydrogen) fluorides by the reaction of KF[66] or Me_4NF[67] with HF. With KF, the products have the stoichiometry KF.2.5HF and KF.3HF. X-ray analyses at -100°C show that they are basically ionic, containing new anions of the general formula $H_nF_{n+1}^-$. The occurrence of these anions is related to the presence of strong F-H...F hydrogen bonds. The poly(hydrogen) fluoride, KF.2.5HF, is in fact K2[H2F3][H3F4] with two distinct and different homologous anions, (7) and (8), whereas KF.3HF has the structural formula KH_3F_4 where the $H_3F_4^-$ anion (9) is an isomer of the $H_3F_4^-$ anion in $K_2[H_2F_3][H_3F_4]$.



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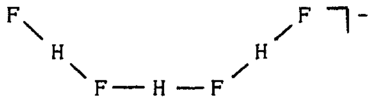

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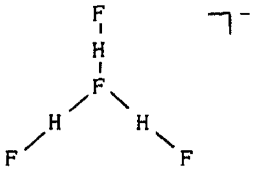
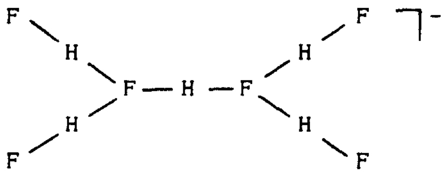


(9)

Mootz et al.[67] have also constructed a phase diagram for the Me_4NF/HF system between 50 and 100 mole% HF. Evidence for the existence of four compounds of the general formula $Me_4N.xHF$ (x = 2,3,5,7) was given. The structures of the low temperature form of $Me_4NF.2HF$ (stable below 83°C), the high temperature form of $Me_4NF.3HF$ (above -87°C) and $Me_4NF.5HF$ have also been determined. All are poly(hydrogen) fluorides containing the $[H_2F_3]^-$, $[H_3F_4]^-$ and $[H_5F_6]^-$ anions respectively, the latter being isolated for the first time. The structures of the $[H_2F_3]^-$ and $[H_3F_4]^-$ anions are similar to those described above, although the



(10)

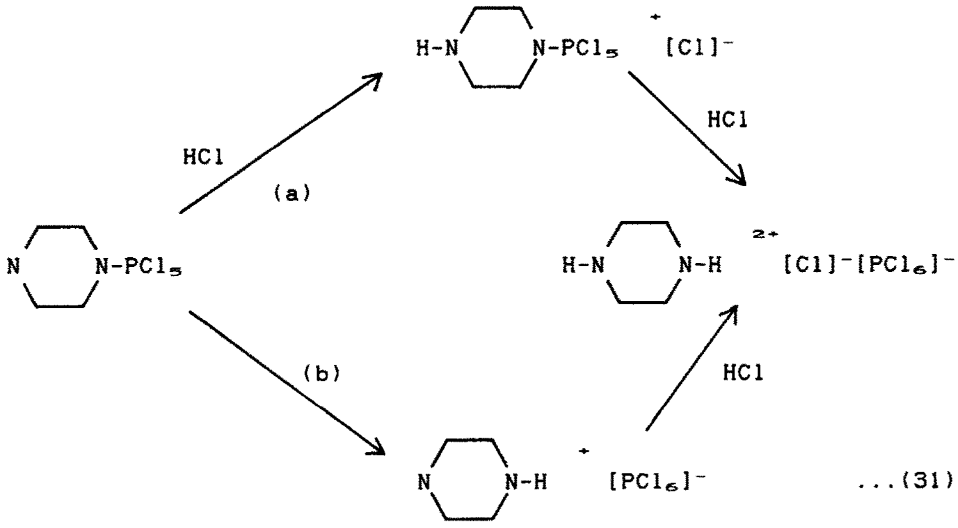
hydrogen bonds in the $Me_4NF.xHF$ cases are somewhat shorter as a consequence of weaker cation-anion interactions. The structure of $[H_5F_6]^-$, shown in (10), contains very short central F-H-F bonds (226.6pm) and four equivalent terminal bonds

(248.4pm).

Mixtures of $H^{18}F$ and Sb_2O_3 have been used as selective radiofluorinating agents to dope trihalogenomethyl groups in 20-50% yield.[68] The overall reaction (equation 30) produces SbF_3 but this is not involved in the doping process. The

$$6HF + Sb_2O_3 \longrightarrow 2SbF_3 + 3H_2O \qquad \ldots(30)$$

reaction of gaseous HCl, DCl or HBr with pyrazine-phosphorus(V) chloride is shown in equation (31).[69] For HCl, the reaction follows route (a) rather than route (b), a conclusion based on results obtained from ^1H n.m.r., infra red and Raman spectroscopy



...(31)

along with information from tensimetric titrations.

Matrix isolation infra red spectroscopic studies in argon of the structures of HI and DI show that both monomeric and dimeric species are present.[70] Reaction with water produced 2:1 and 1:1 complexes, while the reaction of HI with HX (X = Cl,Br) or atomic iodine gave binary complexes.

7.2 HYDROGEN

7.2.1 The Element

Heterogeneous catalysis has been employed to produce NH_3 from H_2 and N_2 at room temperature and atmospheric pressure.[71]

The catalytic medium used is solid potassium-containing ruthenium on active carbon. However, the activity of this catalyst is only 0.011 mmol of NH_3 per day and gram of catalyst, compared with the activity of nitrogenase which can produce NH_3 at a rate of 0.25 mmol per minute and gram of catalyst.

The rate of conversion of syn-gas has been enhanced by the addition of solid K_2O to a Ru-K-Al_2O_3 catalyst.[72] F.t.i.r. spectroscopy showed the presence of KH on the surface, which in turn reacts with carbon monoxide, equations (32) and (33).

$$K_2O_{(s)} + 2H_{2(g)} \rightleftharpoons KH_{(s)} + H_2O_{(g)} \qquad ...(32)$$

$$KH_{(s)} + CO_{(g)} \rightleftharpoons KCH(O)_{(s)} \qquad ...(33)$$

7.2.2 Protonic Acids and Hydrogen-Bonding

The hydrogen bond energy in $(CH_3F)_2H^+$ has been determined from pulsed electron beam high pressure mass spectroscopic data.[73] Direct termolecular clustering of CH_3FH^+ with CHF_3 was not examined due to the occurrence of a rapid nucleophilic displacement reaction (equation 34). For this reason, the experimental method employed was to determine the hydrogen bond energy in $(SO_2)_2H^+$ and then carry out successive displacement reactions of SO_2 by CF_3. This gave in conjunction with the proton affinities of CH_3F and SO_2, a hydrogen bond energy of 32 ± 2 kcal.mol^{-1}, which shows good agreement with the ab initio calculations for $(HF)_2H^+$.

$$CH_3F + CH_3FH^+ \rightleftharpoons (CH_3)_2F + HF \qquad ...(34)$$

Hydrogen bonding in several acid salts of 4,5-dichloro-, 3,6-dichloro- and 3-fluorophthalic acids has been studied by i.r. spectroscopy and X-ray structural analysis.[74] In $NH_4H[3,6\text{-}Cl_2C_8H_2O_4]$ and $KH[3\text{-}FC_8H_3O_4]$, the O...O separations are 247 and 254.1pm respectively, both compoumds being Speakman's Type B_2 dicarboxylic acid salts. In hydrated $NH_4H[3,6\text{-}Cl_2C_8H_2O_4]$, there is a short hydrogen bond (253pm) to the hydrate water molecule. In $Bu_4NH[4,5\text{-}Cl_2C_8H_2O_4]$ the bond length is even shorter at 234pm. Eighteen crystalline benzoic acid heterodimers have been prepared for the first time and characterised by conventional analysis, ^1H

n.m.r., m.p/composition phase studies and X-ray powder diffraction.[75]

New acid polyhydrates, $HPF_6.7.67H_2O$, $HBF_4.5.75H_2O$ and the known $HClO_4.5.5H_2O$ have been studied by low temperature X-ray and differential thermal analysis.[76] These compounds are the first examples of hydrates of strong acids possessing the type 1 or cubic 12A crystal structure of the polyhedral clathrate hydrates. Due to crystal disorder however, the only accurate structure determination is for the HPF_6 hydrate. Thermal analysis of the HBF_4-H_2O system showed the existence of three crystalline hydrates $HBF_4.nH_2O$ (n = 3.5,4,5.75).

Analysis of $[NPr^n{}_4]_2\{[PtCl_4].cis[PtCl_2(NH_2Me)_2]\}$ [77] by neutron diffraction at -20°C show the compound contains N-H..Cl and N-H..Pt hydrogen bonds, of length 231.8 and 226.2pm respectively. The near linear geometry of the Pt..H-N linkage is said to be indicative of 3c-4e bonding.

A discrete rhenium trigonal cluster anion has been found in $NH_4[Re_3Cl_{10}(H_2O)].2H_2O$, formed by crystallising mixtures of $ReCl_3$ and NH_4Cl in HCl.[78] An X-ray structure points to the presence of very strong Cl..H-OH bonds with a Cl..O contact of only 286pm. The cation also forms strong N-H..O bonds, and has seven chlorines as nearest neighbours, along with one of the water molecules of the cluster. The N..O separation is 271pm.

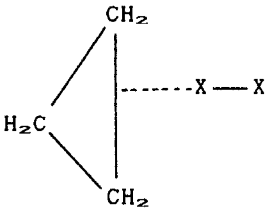
A study into the vibrational spectra of various amines and amine complexes has been carried out by Christe and Wilson.[79] The results for HNF_2 and DNF_2 show that both compounds are associated through H-bridges between the N-atoms in both the liquid and solid states. Adducts formed with KF, RbF and CsF, show Raman evidence for the presence of strongly hydrogen bridged $[F...HNF_2]^-$ anions. For adducts with the latter two fluorides, there is also evidence for the existence of a second modification of the $[F...HNF_2]^-$ anion, with a much stronger bridge.

Hydrogen bonding between the hydrogen halides and various inorganic and organic bases has continued to generate much interest. The structure of the $H_2CO.HCl$ adduct has been investigated by microwave spectroscopy, showing the presence of a non linear H-bond between the oxygen atom of H_2CO and the hydrogen of HCl.[80] A study into hydrogen bonding between HNC, HPC, FCN, ClCN and BrCN with HX (X = F,Cl,Br) via Gaussian orbital SCF-MO calculations has shown that both hydrogen bond strength and molecular geometry depend on the nature of the proton donor.[81]

H-bonded complexes of Me_2O and Me_2S with HF have been prepared by condensing the reagents in argon at 12K.[82] I.r. evidence suggests that bonding in $Me_2S...HF$ is weaker than in $Me_2O...HF$. The relative weakness of the H-bond in the former is said to be due to the diffuse electron density around sulphur, even though the sulphide base has the higher proton affinity. Ault and Sass[83] have reported the formation of weakly held hydrogen bonded complexes between Bu^tX and HX (X = Cl,Br) by twin jet codeposition in an argon matrix at 12K. Evidence for complex formation comes from a shift of ν(H-X) to lower wavenumber (100-200cm^{-1}), along with changes in the vibrational modes of the base. With single jet codeposition, which allows gas phase equilibria to be achieved prior to condensation, halogen exchange occurs when the halogen of HX is heavier than the halogen of Bu^tX. A gas phase reaction is proposed.

Infrared matrix isolation spectroscopy has also been used to isolate and characterise the complexes formed between HX (X = Cl,Br) and substituted cyclopropanes which contain an electron withdrawing substituent.[84] In each case, infrared evidence points to complexes in which HX is bonded to the substituent, rather than to the cyclopropane ring.

Single and twin jet deposition along with matrix isolation techniques have been employed to investigate the reaction of Cl_2, ClF and Br_2 with cyclopropane and its derivatives.[85] I.r. data points to the isolation of a 1:1 complex with interaction occurring at the midpoint of one of the C-C bonds (<u>11</u>).



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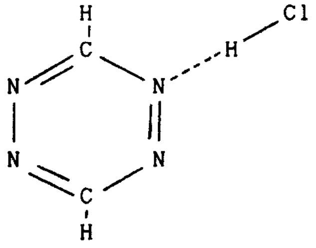
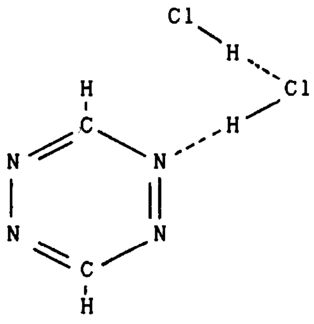


(<u>12</u>)

Hydrogen bonded omplexes between cyclopropyl derivatives containing a π substituent and HF, HCl, DCl or HBr have been isolated and analysed using infrared matrix isolation spectroscopy.[86] The H-X stretching modes show low wavenumber shifts characteristic of H-bonding. Single complex formation has been proposed, with interaction occurring between HX and the π substituent. The large shifts are rationalised in terms of conjugative effects.

Supersonic free-jet expansion has been used to record the laser induced fluorescence spectra of complexes formed between HCl and s-tetrazine.[87] Analysis of the rotational fine structure gave a planar structure for the 1:1 complex with the hydrogen from HCl bonded to the lone pair on a nitrogen of s-tetrazine (12). In the 1:2 complex, the second HCl molecule bonds to the first HCl and not directly to the tetrazine ring. The resultant geometry is however unclear. Two possible structures (13) and (14) were proposed. In this case, structures intermediate between these two extremes are consistent with the observed spectrum. Also consistent was the case where both HCl molecules bonded directly to the ring.



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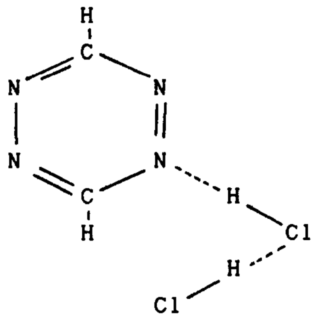

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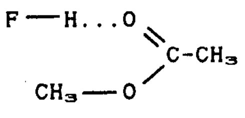
Various hydrogen bonded complexes between HF and several organic compounds have been described by the Andrews research



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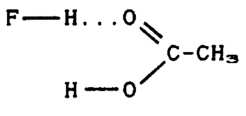
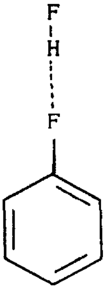


(16)

group.[88] Condensation of HF with acetic acid or methyl acetate with argon at 10K gives the complexes (15) and (16), which were analysed by infrared spectroscopy. Identical methods produced complexes of halobenzenes and HF,[89] including a planar C_6H_5-F...HF complex (17), and two different C_6H_5X...HF complexes (X = Cl,Br), one involving H-bonding to the halogen (18) and one showing H-bonding to the aromatic ring (19). On warming the matrix, complexes of the type



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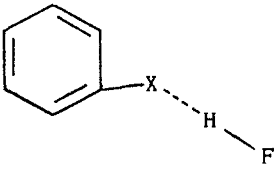

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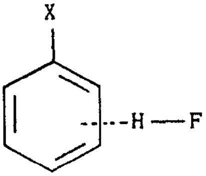
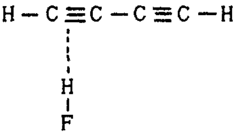


(19)

C_6H_5-X...$(HF)_2$ where X = Cl,F or Br were produced.

The same isolation technique has been used to investigate the interaction between diacetylene and HF.[90] Two primary 1:1 complexes were produced, the first characterised as a π-complex with interaction perpendicular to the triple bond (20) and the second as a δ-complex with interaction at hydrogen (21). Both



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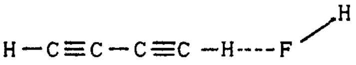
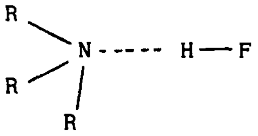


(21)

1:1 (22) and 1:2 complexes (23) have been obtained from methyl substituted amines and HF in an argon matrix.[91] The relative yield of 1:2 complexes increased substantially with methyl substitution.



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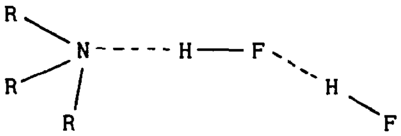

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7.2.3 Hydrides and Dihydrogen as a Ligand

The addition of gaseous hydrogen to MBu^n (M = Li,Na or K) yields the corresponding alkali metal hydride, compounds ideal for the formation of carbanions as only H_2 is given as a by-product.[92] However, these hydrides are not normally reactive, but production by this method gives not only reactive hydrides, but hydrides which deprotonate more selectively.

All the Li_nH_m series of hydrides and monocations have been structurally analysed by ab initio calculations.[93] The results predict stability for the planar LiH_3 and $Li_2H_3^+$ along with the "kite" structural form of Li_3H^+. In a reinvestigation of the BaH_2 structure, via a neutron diffraction study of BaD_2, the powder data analysed showing hydrogen positions corresponding to those in CaD_2, in contrast to an earlier suggestion. The compound is classified as being of the $PbCl_2$ structure type.[94]

In a study of H_2/ML_5 (d^6) interactions by extended Huckel calculations, bonding both as dihydrogen and dihydride has been covered.[95] Bonding as μ_2-dihydrogen is an exothermic process and the most favourable interaction occurs when L is a pure σ donor (L = H^-) rather than a π aceptor (L = CO). This is related to the ability of ML_5 to populate the σ^*H_2 orbital. Coordination as a dihydrate is more favourable for metals such as tungsten with high lying d orbitals than for iron. Replacing δ donor ligands by π acceptors is energetically unfavourable in this case. The position of a π acceptor ligand is also crucial, for example a CO group trans to an incoming H_2 favours the μ_2 mode of bonding. Bonding of hydrogen to d^6 metal complexes has also been investigated using ab initio electronic wave functions and relativistic effect core potentials.[96] The influence of electronic properties of the ligands in the stability of the μ_2 and dihydride forms is discussed.

Rhodium(III) complexes with the general formula $[Cp''Rh(ppy)_3L]_n{}^+$, where ppy is an oligopyridine ligand such as bipy, L = H_2O,Cl^-,Br^-,I^-; and n = 1,2, can in the presence of sunlight and colloidal TiO_2 bring about the photoreduction of H^+ to H_2.[97] The complexes are reduced via Rh(II) to Rh(I), but can be transformed to Rh(III) via evolution of H_2. This reaction mechanism was investigated by cyclic voltammetry, pulse radiolysis and transient absorption spectroscopy.

The most hydride rich cluster yet reported has been prepared, equation (34), by Sutherland et al.[98] The reasons given for

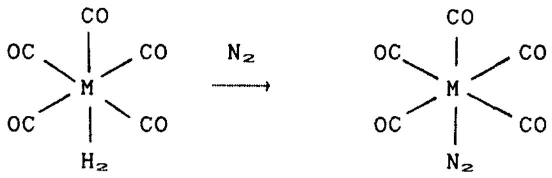
$$[Re_2H_8(PMe_2Ph)] + {}^1/_2[Ph_3PCuOBu^t]_2$$

$$\downarrow C_6H_6$$

$$[Re_2CuH_7(PMe_2Ph)_4] + Bu^tOH + PPh_3 \qquad ...(34)$$

formation of the product are the strong Cu-H (193-200pm) and Cu-Cu (252.7pm) interactions.

Photolysis of $M(CO)_6$ (M = Cr,Mo and W) and H_2 in liquid xenon at -70°C yields $M(CO)_5(H_2)$ while for Cr and W substitution of a second hydrogen molecule is also possible to give cis-$M(CO)_4(H_2)_2$.[99] The three $M(CO)_5H_2$ species have been fully characterised by infrared spectroscopy using ^{13}CO data, C-O factored force field analysis and shifts in ν(H-H). The reactions shown in equations (35)-(38) have also been carried out in liquid xenon at -70°C and the products analysed by similar infrared techniques. For reaction (36), the cis-product is given exclusively, the reaction proceeding via a detectable intermediate, probably cis-$Cr(CO)_4(H_2)(N_2)$. Reaction (37) gives exclusively $Cr(CO)_5D_2$ not $Cr(CO)_5HD$ but the latter is obtained in reaction (38) probably as a result of the isomerisation reaction (39).



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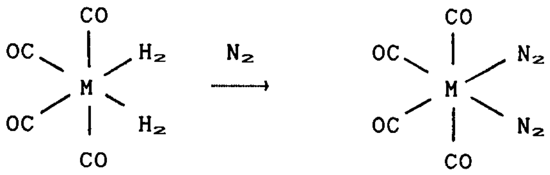

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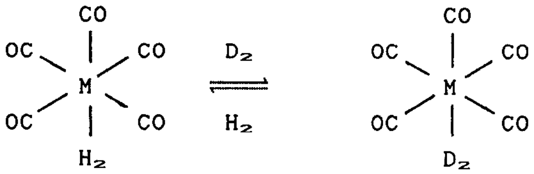

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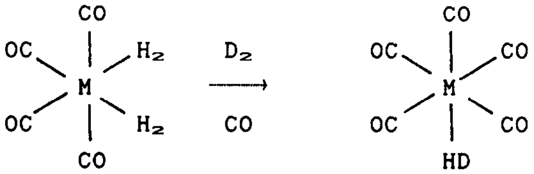

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$$Cr(CO)_4(H_2)(D_2) \rightleftharpoons Cr(CO)_4(HD)_2 \qquad ...(39)$$

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