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Chapter 7

THE HALOGENS AND HYDROGEN

M.F.A.Dove

7.1 HALOGENS

7.1.1 The Elements

Rose and Marier[1] have published a critical report on the major sources and effects of industrial and commercial fluorides that are being dispersed into the atmosphere, water, soil and vegetation. They have assessed the cumulative impact on our environment and cite evidence for widely different levels of tolerance to fluoride in the human diet.

The rate constant k_1 for reaction (1) in the temperature range

$$F + O_2 + M \longrightarrow FO_2 + M \qquad ...(1)$$

223 to 293K and in the presence of Ar has been measured by e.s.r. spectroscopy.[2] The results are consistent with

$$k_1 = (1.0 \pm 0.3)10^{14}\exp(1800/RT)\ cm^6 mole^{-2} sec^{-1}$$

and this agrees well with the rate measured earlier by Arutyunov et al. using a similar method. An apparent induction period for the reaction between Cl_2 and F_2 in copper and fluoroplastic reactors has now been ascribed to the presence of an impurity in the fluorine.[3,4,5] Direct fluorination of $CF_3S_2CF_3$ to CF_3SF_3 has been accomplished by Lagow's method in 90% yield;[4] the reaction at -120°C in a 4-zone reactor required 38h. Reactions of molecular fluorine with small hydrocarbon molecules in F_2 and Ar-F_2 matrices have been described.[5] Certain hydrocarbons, e.g. CH_4, C_2H_2, C_6H_6, could be condensed into the pure F_2 matrix without reaction. Ethylene and allene were similarly inert except when exposed to light ($1 < \lambda < 4\mu$) when C_2H_4 yields 1,2-*gauche*- and *trans*-difluoroethane or vinylfluoride : propylene, butadiene and cyclohexane react spontaneously with F_2 in low-temperature matrices.

Since no accurate measurements at the 10^{-12}v/v level (p.p.t.) of halogenated hydrocarbons have been previously undertaken in Asia, Makide et al.[6] have initiated a systematic survey of the atmospheric concentrations of CCl_2F_2, CCl_3F, CCl_2FCClF_2, CH_3CCl_3, CCl_4, $CHCl{=}CCl_2$, and $CCl_2{=}CCl_2$ over Japan in both remote and urban areas. The data are reproduced in Table 1; sample no.1,taken on a coastal cliff site, shows levels comparable with those of northern hemisphere background concentrations measured in the continental North America. If stratospheric SO_2 concentrations are 2×10^{-10}v/v then Strattan et al.[7] have suggested that reaction (2) (M = Ar, N_2

$$Cl + SO_2 + M \longrightarrow ClSO_2 + M \qquad \ldots(2)$$

or SO_2) is probably not an important sink for stratospheric chlorine in our atmosphere.

Chlorine-37 enrichment occurs in the aqueous phase of a heterogeneous system consisting of a strongly basic anion exchanger and a concentrated fluoride solution.[8] Chromatography has been used to determine the extent of chlorine isotope separation as a function of the concentration of F^- and of the counter ion. The vapour pressure of chlorine has been remeasured in the temperature ranges 206 to 270K and 334 to 417K.[9] In the lower range the new data are in good agreement with Giauque and Powell's (1939) results: in the upper temperature range the new data are considerably higher than Pellaton's (1915) results. An XPS investigation of the reaction between chlorine atoms and molecules and cooled sulphuric acid has shown that Cl^- and higher oxidation states of

Table 1. Atmospheric concentrations (p.p.t.) of halogenated hydrocarbons in Japan.

Sample	Sampling Location*	Date	CCl_2F_2	CCl_3F	$CCl_2F-CClF_2$	CH_3-CCl_3	CCl_4	$CHCl=CCl_2$	$CCl_2=CCl_2$
No.1	Katsuura (Chiba-pref.)	July 22 1978	268	159	25	96	104	2	7
No.2	Mt. Fuji (Yamanashi-pref.)	July 8 1978	335	193	37	269	108	106	66
No.3	Kirizumi (Gunma-pref.)	Dec. 1 1977	316	207	41	599	93	573	163
No.4	Hakone (Shizuoka-pref.)	Dec. 9 1977	360	215	43	841	102	768	195
No.5	Tokyo Tower (Tokyo)	July 7 1978	962	372	234	10100	342	3950	719

* All located between latitudes 35°N and 37°N.

chlorine are generated, whereas with ice only Cl^- is formed.[10]

Lindeman and Forsén[11] have surveyed briefly recent developments in the application of Cl, Br and I nuclear magnetic resonance spectroscopy to chemical and biological systems.

Highly excited and potentially reactive iodine atoms $I(5p^4 6s, {}^2P_{3/2})$ are produced by U.V. multiphoton excitation of CD_3I at 193nm with a rare gas-halogen exciplex laser.[12] The process of photodissociation of the van der Waals molecules I_2He_n, n = 1, 2 or 3, has been studied.[13] It was found that for each molecule the first observed dissociation channel involves the loss of n vibrational quanta from the I_2 stretch.

The X-ray photoelectron and Raman spectra of iodine-doped polyacetylene $((CHI_x)_n$ films, 0.1mm thick, has been obtained and discussed.[14] It was concluded that iodine is more concentrated in the surface region than in the bulk when the value of x is small (< 0.05). Single crystals of a new complex of perylene, P, with I_2, $P.4I_2$, have been grown by an isothermal diffusion technique.[15] Direct current conductivity measurements were made which show that this phase exhibits a metallic temperature dependence over the temperature range 235 to 340K. A typical $\sigma(300K)$ value for these crystals is $40\Omega^{-1}cm^{-1}$. Manometric measurements in the range 40^o to 140^oC and a supplementary aqueous electrochemical technique have been employed to measure the vapour pressure of the iodine complexes of six polynuclear aromatic hydrocarbons, including perylene and coronene.[16] The enthalpy and entropy of formation data calculated from these results fall into two categories; that for which the data resemble the heat and entropy of condensation of gaseous to liquid iodine and that for gas-solid transformation.

A study of the electrical resistivity-composition isotherms of mixtures of iodine and aromatic compounds has indicated the existence of several low resistivity complexes.[17] The thermodynamics of formation of five solid molecular complexes of iodine have been determined electrochemically.[18] All were found to have an enthalpy of formation in the range -5 to -14 kJ mol^{-1} except for the pyrene complex (-1.5 kJ mol^{-1}). The relative stability of the complexes was largely controlled by the standard entropy of formation, which ranged from +16.8 $JK^{-1}mol^{-1}$ for the o-tolidine complex to -21.0 $JK^{-1}mol^{-1}$ for the N-methylphenothiazine complex. Morachevskii has discussed the temperature dependence of charge transfer transitions of iodine complexes and has tested the theory experimentally using the I_2-sec-BuOH system.[19]

7.1.2 Halides

Winfield et al.[20] have used ^{85}Kr to determine the surface areas of CsF, TlF and RbF by the B.E.T. method. The surface areas of CsF and TlF samples are increased markedly by heating in vacuo or by reaction with hexafluoroacetone in MeCN. The solubilities of NaF and LiF in anhydrous MeOH have been determined by means of the fluoride ion selective electrode.[21] The memory effect response time of such electrodes has been investigated by Umezawa and coworkers,[22] who have discussed its significance in analytical problems. Cartwright and Woolf[23] have described a rapid potentiometric titration for fluoride ion using cerium(III) chloride as the titrant with a glass electrode as the indicator system. The F^- concentration should lie in the range 0.002 to 0.02M and the pH should be adjusted initially to 6.3 ± 0.05. The equivalence point is obtained from the pH-titrant volume curve. The procedure as described is claimed to be as precise as that involving the fluoride sensitive electrode.

Carbon powder fluorinated with F_2 in the presence of O_2 is the cathode active material and lithium metal the anode in a battery with a good shelf-life and good discharge characteristics.[24] In a continued study of fluorine-exchange reactions on K_2SiF_6 the importance of an active KF and silicon-component has been demonstrated by Kolditz et al..[25] Mixed hexahaloosmate(IV) anions, such as trans-$[OsFCl_4I]^-$, have been prepared by Shukla and Preetz from the ion-pair reaction between trilaurylammonium fluoride, (TLAH)F, and $(TLAH)_2[OsCl_5I]$ in non-polar solvents.[26]

The carboxy carbons of neat liquid carboxylic acids display an anomalously large nuclear Overhauser effect in ^{13}C n.m.r. spectroscopy that is further enhanced by the addition of KF: the rationalisation is based on the formation of strong hydrogen bonds between F^- and the acid hydroxy group.[27] Four stable crystalline oxime solvates of tetra-n-butylammonium fluoride, of the general type $Bu_4NF.2oxime$, have been prepared and characterised.[28] The spectroscopic changes accompanying solvate formation were interpreted on the basis of strong H-bonding between F^- and the oxime hydroxyl group. A mixture of tetra-n-butylammonium chloride and $KF.2H_2O$ in MeCN can be used as a convenient source of active F^- in the place of tetra-alkylammonium fluorides or KF-crown ether combinations.[29] Surprisingly the use of anhydrous KF in the place of the dihydrate was not as effective in certain reactions. Hydrogen bond assisted C- and O-alkylations, sulphenylations and Michael additions have been carried out with the aid of fluoride ion immobilised on strongly basic anionic exchange resins.[30] Miller et al.[31] have shown that Et_4NF in DMF promotes the alkylation of phenols by MeI, EtI or $PhCH_2I$ to provide good yields of alkylphenylethers, even when the phenol is sterically hindered, bears nitro-groups or is intramolecularly hydrogen bonded. The authors assume that the F^--phenol system behaves analogously to the F^--carboxylic acid system, which is a known source of carboxylate anion. Bouma and Radom[32], however, argue on the basis of an *ab initio* M.O. study that "the H---F bond in the carboxylic acid-fluoride system should not be considered a hydrogen bond." They prefer to describe the $HCO_2H{-}{-}{-}F^-$ interaction as one between HCO_2^- and HF for which they calculate a value of 139kJ mol^{-1}, see Figure 1. They propose that in general the energy of complexation

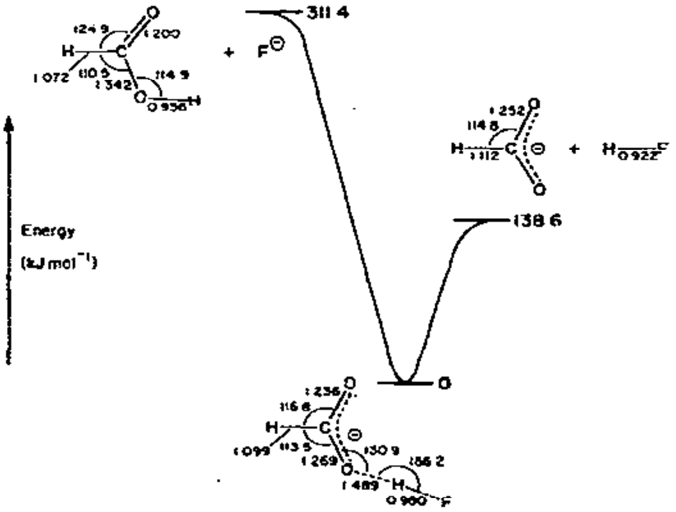
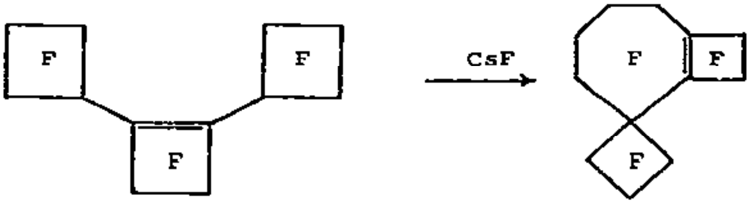


Figure 1. 4-31G optimised structures and relative energies for $[HCOO\cdots H\cdots F]^-$ systems. Bond lengths and angles in Å and degrees (reproduced by permission from Chem. Phys. Lett., 64(1979)216).

or the hydrogen bond energy should be determined as the energy of the complex relative to that of the lower energy set of components.

The results of an investigation of the isothermal (25°C) solubility in the KF-DMSO-$MeCO_2H$ system show that the solubility of KF increases with increasing acetic acid concentration:[33] the solvated products were shown to be $KF.MeCO_2H$ and $KF.2MeCO_2H$. Solvated alkaline earth difluorides $MF_2.2HCO_2H$, M = Sr or Ba, have been isolated from aqueous solution.[34] Their i.r. spectra are said to be consistent with the presence of hydrogen bonding between fluorine and the formic acid molecules. Chambers and coworkers[35] have reported that CsF in DMF catalyses the rearrangement of perfluorocyclobutene trimer (1) to the seven-membered ring system (2) in 83% yield at room temperature.



(1) (2)

Ion cyclotron resonance techniques have been used to examine the formation and reaction of negative ions derived from WF_6.[36] Electron transfer reactions are consistent with a value of 3.5 ± 0.1eV for the electron affinity of WF_6. Fluoride ion transfer reactions suggest the sequence of bond dissociation energies with the value

$$D(SiF_4-F^-) < D((WF_6-F^-) < D(BF_3-F^-)$$

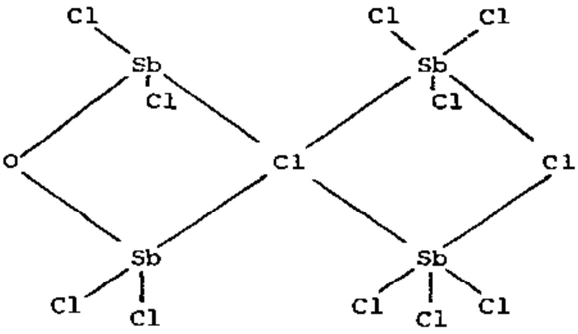
for $D(WF_6-F^-) = 69 \pm 5$ kcal mol^{-1}. Double halide ion affinities corresponding to reaction (3) have been calculated from lattice

$$MX_4(g) + 2X^-(g) \longrightarrow MX_6^{2-}(g) \qquad ...(3)$$

energy studies for a wide range of elements.[37] Acceptor powers towards Cl^- are as follows:

$$\begin{array}{ccccccc} \mathrm{TiCl_4} &&&&&& \\ \wedge &&&&&& \\ \mathrm{ZrCl_4} & < & \mathrm{NbCl_4} & < & \mathrm{MoCl_4} && \\ \wedge && \wedge && \wr\wr && \\ \mathrm{HfCl_4} & > & \mathrm{TaCl_4} & > & \mathrm{WCl_4} & > & \mathrm{OsCl_4} \end{array} \qquad \begin{array}{ccc} \mathrm{GeCl_4} && \\ \vee && \\ \mathrm{SnCl_4} & > & \mathrm{TeCl_4} \\ \wedge && \\ \mathrm{PbCl_4} && \end{array}$$

The product of the photolytic reaction between $SbCl_3$ and ferrocene in benzene, in the presence of O_2, has been characterised by X-ray crystallography and shown to contain an octameric unit, $[Sb_4Cl_{12}O]_2^{4-}$.[38] This anion is unusual on several accounts and especially because of the quadruply bridging chlorine atom in each pair of the $Sb_4Cl_{12}O$ half units (3).



(3)

The electrochemical oxidation of Br^- in DMSO, MeCN, or DMF occurs by a two-step process. In the presence of DMSO the current associated with the second step is anomalously large.[39] The authors attribute this to the formation of a Br_2-DMSO complex whose oxidation occurs at the same potential as that of the second step of the Br^- ion oxidation. The equilibrium constant for reaction (4) has been shown to be 12.2 ± 2.4 at 321°C by U.V. spectrophotometry.[40] The bond dissociation energy D(Me_3Si-I) was

$$Me_3SiI \;+\; HBr \rightleftharpoons Me_3SiBr \;+\; HI \qquad \ldots(4)$$

hence estimated to be 322kJ mol^{-1}.

7.1.3 Interhalogens and Related Species

The review by Shamir[41] of the polyhalogen and interhalogen cations supercedes that published by Gillespie and Morton in 1971. Andrews[42] has reviewed the spectroscopy of $Cs^+Cl_2^-$ produced in inert matrices. The heat of formation of Cl_3^- in the gas phase has been estimated to lie between -72.7 and -82.8 kcal mol^{-1} from the results of a mass spectrometric study of the negative ion-molecule reactions in SO_2Cl_2.[43] In an attempt to resolve the controversy among experimentalists about the geometry of the Cl_2F^+ cation, *ab initio* calculations have been carried out on the ground states of $ClFCl^+$ and $ClClF^+$. Joshi and Morokuma[44] find that the symmetrical cation is the more stable. They have also calculated that $HFCl^+$ is more stable than $HClF^+$.

The effect of ozone on the rate of formation of ClF has been investigated in nickel, copper and p.t.f.e. reactors.[45] Petrov et al. report that under their conditions the presence of a trace of ozone (0.003%) inhibits the rate of reaction between Cl_2 and F_2 at 197K: on the other hand HF was found to exert a catalytic effect. The appearance potentials and excess kinetic energies of the ions generated from ClF_3 have been measured mass spectrometrically.[46] The reaction of graphite with a solution of CsF in ClF_3 leads to the formation of $C_4F.ClF_3$.[47] This new, pale yellow product is an insulator and is reported to be stable thermally up to 400°C, inert to the action of water but not towards stronger reducing agents such as NH_3 or aqueous N_2H_4. The reaction of ClF_3 with excess silicon has been studied by Garanin in a sealed reactor at high initial ClF_3 pressures, 19.5, 38.3, and 54.3 kPa.[48] At the lowest pressure the reaction proceeds according to the reaction (5) and at the highest pressure according to (6). The ^{35}Cl n.q.r. spectra

$$Si + 2ClF_3 \longrightarrow SiF_4 + 2ClF \qquad ...(5)$$

$$3Si + 4ClF_3 \longrightarrow 3SiF_4 + 2Cl_2 \qquad ...(6)$$

of $MClF_4$, M = Cs, Rb or K, have been obtained:[49] a marked dependence of the frequency and other derived parameters on the nature of the cation was noted and was attributed to the polarization of the electric field by the cations.

A second polymorph of Ph_4AsBr_3 has been investigated by single crystal X-ray methods:[50] although there is some doubt about the space group (P2/c) for this modification the Br_3^- ion is symmetrical, with Br-Br 2.54Å and BrBrBr angle 178°. Chemiluminescence from electronically excited BrF and IF has been observed from reactions of Br_2, I_2, ICl or HI with O_2F.[51] The reaction of Br_2 with ClO_2 has been shown to be a self-propagating chain reaction which emits red and near i.r. chemiluminescence owing to a triplet-singlet transition of BrCl.[52] A partial rotational analysis of the electronic spectrum of excited BrCl has yielded new spectroscopic constants for BrCl in ground and excited states.

The i.r. spectra of $M^+BrF_2^-$ ion pairs in Ar matrices has been obtained from samples of co-deposited $MF/F_2/Ar$ at 15K.[53] Absorptions due to symmetric FXF^- and asymmetric XFF^- were reported for both X = Br and I. Sulphur dioxide is oxidised by $Br_3^+MF_6^-$, M = As or Sb, to SO_2BrF.[54]

Nesmeyanov et al.[55] have reported the fluorination of aryl bromides to the related BrF_2 derivatives by the action of XeF_2 with BF_3 etherate (or HF) in CH_2Cl_2 (or SO_2). Yields of these reactive intermediates was claimed to be < 10% at -70°C. Chemical evidence was provided by the coupling reaction with arenes to form diarylbromonium salts. The molecular structure of BrF_5 has been refined by a combined analysis of gas phase electron diffraction data and microwave rotational constants:[56] the preferred values are $r_{av}(Br-F) = 1.753(2)Å$, $\Delta r_{av}(BrF_{eq}-BrF_{ax}) = 0.069(6)Å$ and $F_{ax}BrF_{eq} = 85.14(4)°$.

BrF_5 and its complexes with SbF_5, $BrF_5.nSbF_5$ n = 1, 2, 3 and 7, have been studied by ^{81}Br, ^{121} and ^{123}Sb n.q.r. spectroscopy.[57] From the results it was inferred that ClF_5 possesses a greater donor capacity than BrF_5.

Halogens, when added to flames, usually generate negative ions. In addition iodine produces I^+, I_2^+, IO^+ and I^{2+} whereas bromine gives only Br^+ and Br_2^+; on the other hand chlorine forms no positive ions whatsoever. The dominant species are I^+ and Br^+: Burdett and Hayhurst[58] have investigated in detail the disappearance of I^+ from the burnt gases of flames from 1820 to 2650K.

The $[S_{14}I_3]^{3+}$ ion has been produced as the SbF_6^- salt by reaction (7).[59] The X-ray structure shows that the cation comprises

$$3\tfrac{1}{2}S_8 + 3I_2 + 10SbF_5 \xrightarrow{AsF_3} 2[S_{14}I_3][SbF_6]_3.2AsF_3 + (SbF_3)_3.SbF_5 \qquad ...(7)$$

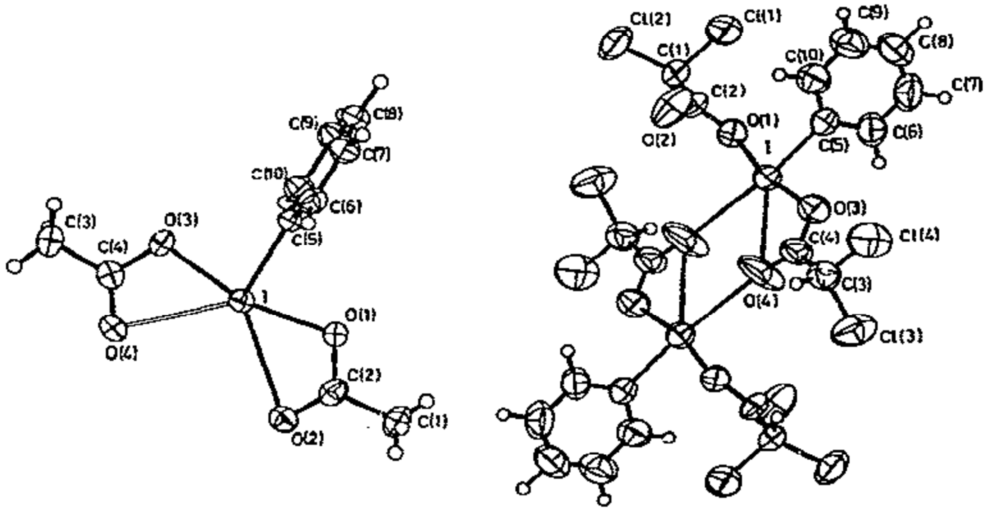
two S_7I^+ cations joined by S through an I at an inversion centre such that the SI distance is 2.67Å. Crystalline penta-iodinium hexafluoroantimonate has been prepared by the reaction of I_2 and SbF_5 in AsF_3.[60] The structure of the product comprises two crystallographically independent planar, bent I_5^+ chains and SbF_6^- ions. The cations are effectively centrosymmetric each with colinear central bonds (2.90Å) and shorter (2.68Å) outer I-I bonds. Three I_5^+ units are joined by a weak (3.42Å) interaction to form what may be regarded as an approximately planar I_{15}^{3+} unit.

The kinetics of the second order reaction of Cl_2 with I_2 in CCl_4 to form ICl have been investigated at 25°C.[61] The reaction of electronically excited ICl with cis- and trans-1,2-dibromoethylene has been studied.[62] Selective excitation of $I^{37}Cl$ using a CW dye laser gave cis- and trans-1-bromo-2-chloroethylenes containing up to 78.4 and 73.9% ^{37}Cl respectively. Iodine(I) chloride oxidises thioureas rapidly and quantitatively, according to equation (8), in the presence of HCO_3^- to neutralize the acid.[63]

$$(RNH)_2CS \;+\; 8ICl \;+\; 5H_2O \longrightarrow (RNH)_2CO \;+\; 4I_2 \;+\; H_2SO_4 \;+\; 8HCl \qquad \ldots(8)$$

The liberated iodine can be titrated with a solution of ICl_3 in hydrochloric acid: this method of analysis can be extended to isothiocyanates, which can be converted to a thiourea by reaction with a primary amine. Solutions of I_2 or ICl in pyridine, 2,6-dimethyl- and 2,4,6-trimethyl-pyridine have been studied by ^1H and ^{13}C n.m.r. spectroscopy.[64] The results support the reported formation of three species : the charge transfer complex B.XI (X = Cl or I), the 1:n complex $BI^+X_nI_{n-1}^-$ and the N-iododipyridinium salt, $B_2I^+X_nI_{n-1}^-$. The ease of formation of each species appears to be a function of the basicity the pyridine (B), of acceptor acidity, solvent polarity and the relative solute concentrations.

The crystal structures of two phenyliodine(III) carboxylates have been determined, at −60°C in order to minimise the decomposition of crystals in the X-ray beam.[65] The diacetate (4) was found to be essentially molecular with unsymmetrically bidentate acetato groups, thus raising the coordination of iodine to pentagonal planar (by O(1)-O(4) and C(5)), see Figure 2. In the bis(dichloroacetate)(5), however, one carboxylato group is unidentate whereas the other group has a unidentate oxygen and a bidentate bridging oxygen. A new reaction of bis(trifluoroacetoxy)phenyliodine(III)

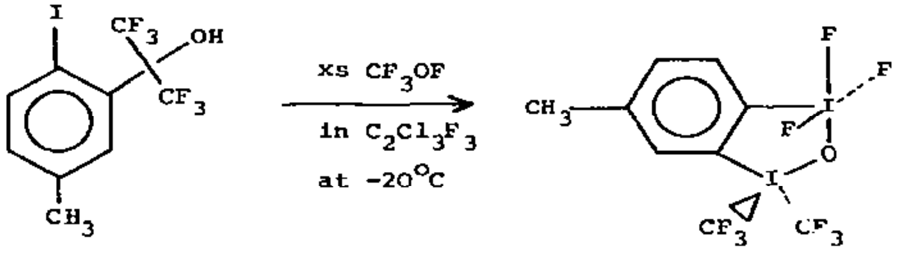


(4) (5)

Figure 2. ORTEP views of diacetatophenyliodine(III)(4) and of bis(dichloroacetato)phenyliodine(III)(5). (Reproduced by permission from J. Chem. Soc. Dalton Trans., (1979)854).

involves the oxidative cleavage of various benzyl ethers into the carbonyl compounds and benzyl (or alkyl) trifluoroacetates.[66]

Alkoxyaryltrifluoroperiodinane (6) is the first example of a stable pentacoordinate organoiodine species containing a simple aryl ligand and an alkoxy ligand bonded to iodine(V).[67] It has been prepared in 95% yield by reaction (9). The product (6, is



...(9)

(6)

stable indefinitely at room temperature and is unreactive towards atmospheric moisture; it is a milder oxidiser than IF_5 and converts primary and secondary amines bearing α-hydrogens to the corresponding carbonyl compounds. The molecular structure of gaseous IF_5 has been derived from electron diffraction data and the published value of the (microwave) B rotational constant.[68] The structural parameters (with 2σ error estimates) are $r_{av}(IF) = 1.860(2)Å$, $\Delta r_{av}(IF_{eq} - IF_{ax}) = 0.034(14)Å$, and $F_{ax}IF_{eq} = 82.1(6)^{\circ}$.

7.1.4 Oxides, Oxide Halides, and Oxoanions

The action of F_2 on a suspension of dry sodium trifluoroacetate in a chlorofluorocarbon at -75°C produces a stable oxidising solution containing approximately 50% C_2F_5OF.[69] Such a mixture acts on steroidal enol acetates to give α-fluoroketones in good yields.[70] Fluorine gas reacts with trifluoroacetic acid or the hydrated sodium salt leading to the formation of trifluoroacetyl hypofluorite.[69] Mass spectra of CF_3OF, $CF_2(OF)_2$, CF_3OOF, CF_3OOCF_3 and CF_3OOOCF_3 have been recorded by Huston and Studier.[71] These workers employed a Kel-F inlet system, such as had been used when characterising HOF; this enabled them to observe the CF_3^+ peak from CF_3OF whereas previous workers had seen mainly COF^+ and COF_2^+. Oxygen-18 tracer studies have shown that the reactions of HO^*F with H_2O, aqueous HSO_4^- and aqueous $[Cr(NH_3)_5N_3]^{2+}$ lead to transfer of oxygen with formation of HOO^*F, O_3SOO^*H, and $[Cr(NH_3)_5NO^*]^{2+}$ respectively.[72]

Fichter's ephemeral oxidising agent, formed when F_2 is passed through aqueous solutions of sulphates or hydrogen sulphate, has been identified by Appleman and coworkers as the SO_4F^- ion, which they have isolated as its Rb or Cs salt.[73] I.r. and Raman spectra of the salts were assigned and they correlate well with the isoelectronic ClO_4F; on this basis the species is described as the fluoroxy or hypofluorite ion, O_3SOF^-. Solutions in MeCN are more stable than those in water : the solid salts decompose at room temperature at the rate of 3 to 5% per month. A single crystal X-ray crystallographic examination of the Rb salt shows that the anion has distorted tetrahedral structure;[74] the O-F distance and the SOF angle are 1.412(10)Å and 107.8° respectively.

Pure fluorine perchlorate, $FOClO_3$, can be prepared in high yield by the thermal decomposition of NF_4ClO_4 and this product can be manipulated more safely than the material prepared in other ways.[75] The addition reaction at $-45^{\circ}C$ with C_3F_6 yields n- and i-C_3F_7 perchlorates in the ratio 2:1. This result suggests that the F-O is of low polarity and does not justify the assumption of a significantly positive character for fluorine.

A one dimensional transport-kinetics model suggests that significant variations in the stratospheric abundance of NO, NO_2, Cl, ClO, OH and HO_2 can be expected during a solar eclipse.[76] Wuebbles and Chang have pointed out that total atmospheric columns of Cl and NO should disappear completely. New measurements of the absorption cross-section of HOCl suggests that this molecule may be more stable to photolysis than had been originally thought.[77] This and recent measurements of the rate of formation imply that significant concentrations of HOCl could form in the stratosphere. The reactions of NO at a partial pressure $\leqslant 1$ torr with OCl^- and HOCl have been investigated.[78] The chain reaction initiated by the endothermic step (10) can account for the data. The exothermic

$$\mathrm{NO(aq)} + \mathrm{HOCl(aq)} \rightleftharpoons \mathrm{HONO(aq)} + \mathrm{Cl(aq)} \qquad \ldots(10)$$

reaction (11) is slower than (10). The overall reaction seems to

$$\mathrm{NO} + \mathrm{ClO^-} \longrightarrow \mathrm{NO_2} + \mathrm{Cl^-} \qquad \ldots(11)$$

offer a promising explanation of reducing NO and NO_2 emissions from industrial plants.

The gas phase reaction (12) has been investigated by U.V.

$$\mathrm{Cl_2O} + \mathrm{H_2O} \rightleftharpoons 2\mathrm{HOCl} \qquad \ldots(12)$$

spectrophotometry from 200 to 500nm at 333K.[79] The equilibrium constant K_{12} was calculated to be 0.132 ± 0.008. The U.V. absorption spectrum of $ClONO_2$ has been reinvestigated over a range of temperature.[80] The new data for cross sections do not affect in a major way the results of O_3-depletion calculations. The kinetics ofreaction (13) have been studied by infrared

$$ClONO_2 + N_2 \longrightarrow ClO + NO_2 + N_2 \qquad \ldots(13)$$

spectrophotometry at 313 and 333K and pressures 1 to 180 torr.[81] No deviation from first order dependences was detected for $p \leqslant 120$ torr. Rate constants for the reverse reaction are ca. 3 times smaller than those obtained from discharge flow measurements.

Katsuhara and DesMarteau[82] report that chlorine(I) triflate, $ClOSO_2CF_3$, adds stereospecifically to the isomers of CFH=CFH and that the displacement of chlorine from the product $CF_3SO_3CFH.CFHCl$ proceeds with retention of configuration. The reaction at low-temperature of the sodium salts of fluorinated carboxylic acids with ClF has been used to prepare several new chlorine(I) compounds – CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, HCF_2CO_2Cl, and $ClCF_2CO_2Cl$ – which have been characterised by i.r., n.m.r., and Raman spectroscopy.[83] $CF_2(CF_2CO_2Cl)_2$ could not be characterised completely owing to its low volatility and explosive decomposition above -10°C.

The complete He(I) p.e. spectrum of ClO has been recorded and interpreted with the aid of ab initio SCF calculations.[84] Of the expected eleven ionic states, five have been positively identified: the remaining six occur over a 1.5eV energy range and contribute to a broad band at 14.68eV. Three bands of ^{35}ClO near 170nm have been photographed at high resolution by Coxon.[85] The rotational assignments identify the transitions as $^2\Sigma^- \leftarrow {}^2\Pi_i$; the spin-orbit coupling constant for the ground state has been determined precisely for the first time. ClO radicals themselves have been shown to decay by three bimolecular reaction routes, (14) – (16).[86]

$$2ClO \longrightarrow Cl_2 + O_2 \qquad \ldots(14)$$

$$2ClO \longrightarrow Cl + ClOO \qquad \ldots(15)$$

$$2ClO \longrightarrow Cl + OClO \qquad \ldots(16)$$

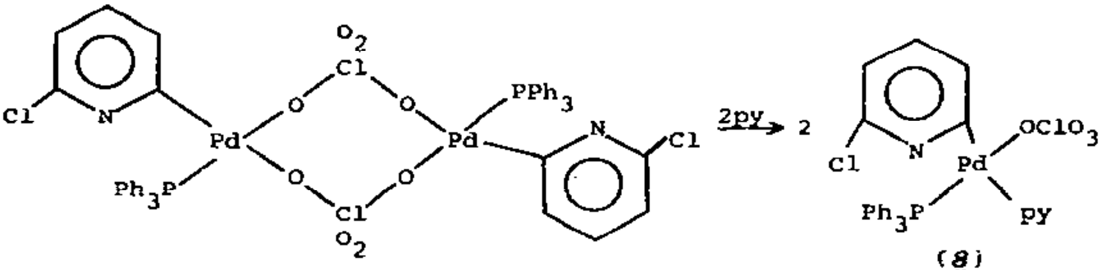
Evidence was also obtained for the formation of a ClOOCl dimer whose stability at 298K is kinetically significant. The low intensity photolysis of $Cl_2 + O_2 + N_2$ mixtures has been reinvestigated by Cox et al.[87] to observe ClO_2 and ClO in the U.V. region. The results substantially confirm the work of Johnston and coworkers. The heat, entropy, free energy and equilibrium constants of aqueous solutions of ClO_2 have been calculated at 25°C.[88] The free energy of formation of ClO_2^- is 27kJ mol^{-1}.

An investigation of the thermal decomposition of $AgClO_3$ indicates that part of the salt is oxidised to $AgClO_4$ and that the final product is AgCl.[89] Chlorate ion can be determined quantitatively by reduction with Cl^- in H_2SO_4 to form Cl_2;[90] the latter reacts cleanly with methyl orange and the decrease in the concentration of the latter can be measured at 504nm.

The standard heat of formation of perchloryl fluoride, $FClO_3$, has been redetermined by calorimetry in aqueous alkaline solutions;[91] the value, -22.6 ± 1.0kJ mol^{-1}, is consistent with previous work which involved hydrogenation. The reaction between ethylenediamine, en, and Cl_2O_7 in CCl_4 at 20°C produces an equimolar mixture of $enH^+ClO_4^-$ and $HN{=}CHCH_2NH_3^+ClO_3^-$.[92] Schilt[93] has published a book entitled "Perchloric acid and the perchlorates". Raman and i.r. spectra of anhydrous orthorhombic $NaClO_4$ have been examined over the range 90-600K.[94] Dynamic interactions between adjacent ClO_4^- ions were very small. Only one mode of the fundamental ν_4 of ClO_4^- showed a chlorine isotope splitting effect.

Anhydrous $HClO_4$ displaces four chlorines from $LiAlCl_4$ smoothly at -30°C provided that the HCl produced is removed from the reaction mixture.[95] The dominant reaction product is $Li_2Al(ClO_4)_5$ according to X-ray diffraction studies and this compound can be made more satisfactorily by the action of $HClO_4$ on a 1:1 molar mixture of $LiClO_4$ and $LiAlCl_4$. The behaviour of $MAl(ClO_4)_4.HClO_4$, M = NH_4, Rb or Cs, $Rb_2Al(ClO_4)_5$ and $Cs_2Al(ClO_4)_5.HClO_4$ towards $HClO_4$ have also been reported.[96]

The effect of hydration on the ion pairs Li^+ClO4^- and $K^+ClO_4^-$ in Ar matrices has been investigated by Draeger et al..[97] The splitting in the components of the ν_3 ClO_4^- i.r. band is reduced by a factor of three on hydrate formation. In the binuclear complex $[Pd(ClO_4)(C_5H_3NCl)(PPh_3)]_2$, (7), the anionic group functions as a bridging ligand.[98] On reaction with pyridine, equation (17), the ClO_4 group remains coordinated but only as a unidentate ligand (8). The tetrafluoroborate and hexafluorophosphate complexes behave similarly.



(7) (8) ...(17)

The rate constant for reaction (18) has been measured:[99] it obeys

$$Br + O_3 \longrightarrow BrO + O_2 \qquad ...(18)$$

the Arrhenius equation over the temperature range 234 - 360K. Bromine or iodine atoms co-condensed on a window at 9K together with NO_2 and an excess of Ar have been shown to form nitryl bromide or iodide, respectively.[100] The planar C_{2v} molecules have been characterised by i.r. spectroscopy; the calculated force constants are in good agreement with the extrapolated parameters for $ClNO_2$ and NO_2. Tevault[101] has also produced $BrNO_2$ in this way: he also reports that photolysis of the matrices with near-U.V. radiation causes the absorptions of the O-bonded isomer, ONOBr to grow.

The kinetics of the reaction of aqueous BrO_2^- with basic aqueous solutions of I^-, SO_3^{2-}, HCO_2^- and $S_2O_3^{2-}$ have been investigated.[102] The reactions all show some dependence on the hydroxide ion concentration: the relative rates parallel those of the corresponding reactions of ClO^- although the rate constants for the $[OH^-]^{-1}$-dependent terms are approximately 10^5 slower for BrO_2^-.

Bromosyl fluoride, $BrOF_3$, has been shown to form 1:1 adducts by direct reaction with BF_3 and AsF_5 in solution in either HF or BrF_5:[103] the AsF_5 and SbF_5 adducts were formed by reaction (19), M = As or Sb. The Raman and ^{19}F n.m.r. spectra of these adducts were

$$MF_5.IO_2F_3 + BrF_5 \longrightarrow IOF_5 + MF_5.BrOF_3 \qquad ...(19)$$

interpreted in terms of ionic structures containing the BrF_2O^+ cation. Decomposition of the BF_4^- and AsF_6^- salts to Br_2^+ (15m and 1h at room temperature) was observed whereas the SbF_6^- derivative formed $BrF_2^+SbF_6^-$ after 10d.

Appleman and coworkers have investigated some reactions of the aqueous perbromate ion, BrO_4^-.[104] Oxygen exchange was shown to be slow, less than 7% at 94°C after 19d, even in basic solution. Reaction rates with a number of two-equivalent reductants were determined and it was concluded that these processes generally involve oxygen transfer : the slowness of such reactions can thus be seen as a reflection of the inertness of BrO_4^- towards removal of its oxygens.

The reaction of nitric acid with phenyliodine(III) derivatives was originally reported in 1892 to give $PhI(NO_3)_2$. However, later investigations have shown that the product is μ-oxo-bis[nitrato-(phenyl)iodine(III)]. The crystal structure has now been determined and the T-shaped arrangement of atoms around iodine has been confirmed.[105] Weaker interactions, both inter- and intramolecular, involving nitrato oxygen atoms increase the coordination number of iodine to five (Figure 3). Iodine(V) oxide reacts as an acid with salts such as K_2CrO_4, Na_2WO_4 and K_3PO_4 and

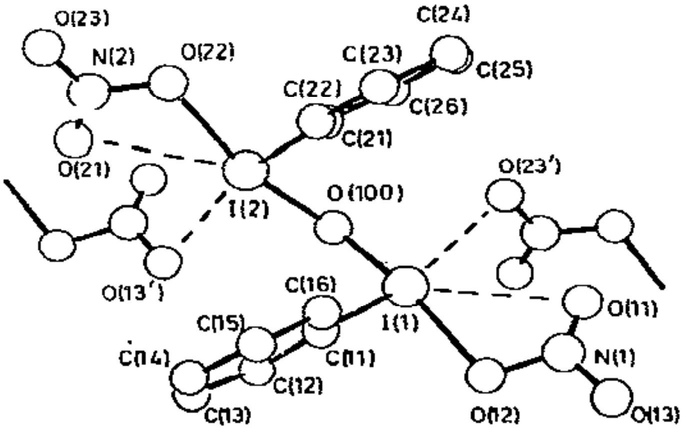


Figure 3. A view of the molecule μ-oxo-bis[nitrato(phenyl)iodine(III)] showing the I---O secondary interactions. (Reproduced by permission from J. Chem. Soc. Dalton Trans., (1979)851).

the reactions can be followed potentiometrically.[106] The standard enthalpy of formation of $CsIO_3$ has been redetermined calorimetrically.[107] The result, -125.39 ± 0.47 kcal mol^{-1}, calculated from a thermodynamic cycle of three reactions, is in reasonable agreement with two earlier determinations. The kinetics of the thermal decomposition of $RbIO_3$ to RbI and O_2 has been studied at 520-560°C.[108] In the vicinity of the melting point the activation energy of the decomposition is 56 kcal mol^{-1}. Solubility in the $Al(IO_3)_3$-$LiIO_3$-HIO_3-H_2O system at 25°C has been investigated. The crystallization fields of HIO_3, α-$LiIO_3$, $Al(IO_3)_3.6H_2O$, $Al(IO_3)_3.2HIO_3.6H_2O$ and the solid solution of HIO_3 and $LiIO_3$ have been determined.[109] The new phase $2KIO_3.Mn(IO_3)_2.2H_2O$, similar to the analogous Zn(II) and Co(II) phases, has been observed in the KIO_3-$MnIO_3$-H_2O system at 50°C.[110] The crystal structure of triclinic $Al(IO_3)_3.8H_2O$ has been solved by Sorokina et al..[111] The ^{127}I n.q.r. spectra of HI_3O_8, DI_3O_8 and I_2O_5 have been described.[112] The data for I_2O_5 differ from those previously reported and this can now be attributed to partial hydration of the samples used by earlier workers.

There have been conflicting views on the interpretation of the U.V. spectrum of IO_4^- in aqueous solution. Buist and Tabatabai[113] have resolved the absorption into two overlapping Gaussian bands at 222nm (ε_{max} 1000 m^2mol^{-1}) and 280nm (ε_{max} 27 m^2mol^{-1}). From solvent shift effects they propose that both arise from intramolecular transitions of the $\pi^*\leftarrow\pi$ and $\pi^*\leftarrow n$ type. The oxidation of I^- by IO_4^- is catalysed by 1,10-phenanthroline iron(III) complexes at pH 4-6. A photocalorimetric study at 582nm and 25°C has indicated the formation of mono- and bis- phenanthroline dihydroxo complexes.[114] Cookson and Stevens[115] have reported that excess concentrated H_5IO_6 must not be used when preparing tetraethylammonium periodate, because of the danger of an explosion.

The first iodine hypofluorite has been made by Christe and Wilson:[116] the compound has been prepared by thermal decomposition of $NF_4^+IO_2F_4^-$. Two volatile iodine-containing species were produced in the ratio 2:1 which were characterised as the <u>cis</u>- and <u>trans</u>-isomers of $OI(OF)F_4$. It has been reported that periodate (as $H_4IO_6^-$) catalyses the exchange of oxygen between arsenate ions and water.[117] The catalytic process was interpreted in terms of the reversible condensation of arsenate and periodate ions to form an arsenatoperiodate.

7.1.5 Hydrogen Halides

Hydrogen bonding in the gas phase between HF and alcohols has been studied by i.r. spectroscopy for the first time.[118] Evidence has been obtained for the formation of 1:1 heterodimers, ROH···HF, for which the vibration wavenumbers $\bar{\nu}$(F-H) have been estimated: in the series H_2O, MeOH and Me_2O these show a stepwise decrease of 75cm^{-1}, thus reflecting the increase in basicity of oxygen in these molecules. McDonald and Klein[119] have reviewed results obtained from computer simulation of the hydrogen bonded liquids HF, H_2O and NH_3. An assessment was made of the relative merits of potentials obtained by fitting gas phase data and solid state properties to quantum mechanical calculations.

Gut[120] has evaluated the autoprotolysis constant of anhydrous HF from potentiometric titrations of solutions of H^+ with F^-. Concentrations of the latter were determined with the help of a silver electrode acting in the presence of HCl and AgCl. The hydrogen electrode's behaviour as an indicator of pH in anhydrous HF or HF-related superacid media has been investigated.[121] The electrode functions reversibly in KF or BF_3 solutions, however, in the presence of TaF_5 the potentials are time-dependent. Both AsF_5 and SbF_5 show more complex behaviour and, indeed, AsF_5 is slowly reduced by H_2 to As(III). Chemical and electrochemical studies of solutions of isopentane in HF-related superacid media have been reported.[122] The two main processes involve protonation of the hydrocarbon and oxidation to the carbonium ion as well as the production of a radical species which then generates polymeric species. The addition of HF to tetra- and trichloroethane and related compounds is catalysed by TaF_5,NbF_5, $TiCl_4$ and $MoCl_5$.[123] Hydrogenation of C_2Cl_4 can also be carried out in HF in the presence of H_2.

Faris[124] has determined distribution coefficients for the adsorption of more than forty elements on anion exchange resins from aqueous solutions containing HCl (0.1 - 12M) and HF (0.1 - 8M). The report also contains an extensive bibliography relating to the use of anion exchangers for fluoride-containing media. A 70% solution of HF in pyridine converts aryl triazenes, Ar-N=N-NR_2, to aryl fluorides, ArF in high yield at temperatures in the range 0 - 80°C.[125] The redox properties of M^{n+}/M or M^{n+}/M(Hg) couples have been investigated in 0 - 60 wt.% HF for M = Cd^{2+}, Tl^+, Sn^{2+}, Ag^+, Pb^{2+}, Hg^{2+} and Hg_2^{2+}.[126]

Molecular motions in crystalline NH_4HF_2 have been investigated by pulsed n.m.r. spectroscopy.[127] The activation energy of the NH_4^+ reorientation was found to be 25.5 ± 1.0 kJ mol^{-1} from the T_1 data, while those of the HF_2^- ion 180° flips were estimated to be about 40 and 60 kJ mol^{-1}, for the non-equivalent ions, from $T_{1\rho}$ data.

Triphenylphosphine oxide yields a mono-HF solvate when recrystallised from 40% aqueous HF:[128] an X-ray structure determination has shown that the compound contains a short H-bond, the O---(H)-F and H-F distances being 2.384(5) and 0.998Å respectively. In the NH_4F-HF-DMSO system, NH_4HF_2 is the solid phase at equilibrium over a wide range of HF concentrations;[129] its solubility increases with increasing HF concentration. The same phase arises over a very limited concentration range in the NH_4PF_6-HF-DMSO system, in which no HF solvate of NH_4PF_6 was discerned.

Matrix photoionisation experiments have been conducted on HF(DF) in an argon matrix and the i.r. spectrum of the isolated HF_2^- ion obtained.[130] A band at 1377.0(965.5) cm^{-1} was assigned to ν_3 of HF_2^- (DF_2^-).

The matrix (Ar, 15K) photoionisation products of chloroform have been studied by i.r. spectroscopy.[131a] The anionic product exhibits isotopic data appropriate for a single H, single C and two equivalent Cl atom species : Br and I substitution (as $CHCl_2Br$ and $CHCl_2I$) data indicate the involvement of a third inequivalent halogen atom. These observations are consistent with the formation of the hydrogen bonded $Cl^-\cdots HCCl_2$ anion as the product of electron capture by $CHCl_3$. Under the same conditions[131b] CHF_3, CHF_2Cl and CHF_2Br generate both $F\text{-}H\cdots(CFX)^-$ and $X\text{-}H\cdots(CF_2)^-$, X = F, Cl or Br, whereas CHF_2I produces $F\text{-}H\cdots(CFI)^-$ and $I^-\cdots(HCF_2)$. Bouma and Radom[32] have carried out ab initio MO calculations on $H_3O^+F^-$, $H_2O\cdots H\cdots F$ and $H_2O.HF$; their results are depicted in Figure 4.

The ^1H n.m.r. spectra of mixtures of ROH (R = H, Me, Et) or HBr in CF_2Br_2-CD_2Cl_2 at -100°C and below show signals at 12-13 or ca. -1.5 p.p.m. which Emsley et al.[132] assign to the species ROH_2^+ or HBr. The 1:2 adduct $Me_2SO.2HF$ is formed by the addition of anhydrous HF to DMSO.[133] The monohydrochloride was also prepared and characterised by analysis, ^1H and ^{13}C n.m.r. spectroscopy. Solutions of Me_4NCl and Me_3NHCl in liquid HCl have been examined by Raman spectroscopy:[134] the solution numbers of Cl^- in these solutions are 6 for ⩽ 3M Me_4NCl, which the ion pairs of Me_3NHCl are apparently solvated by 5 HCl molecules.

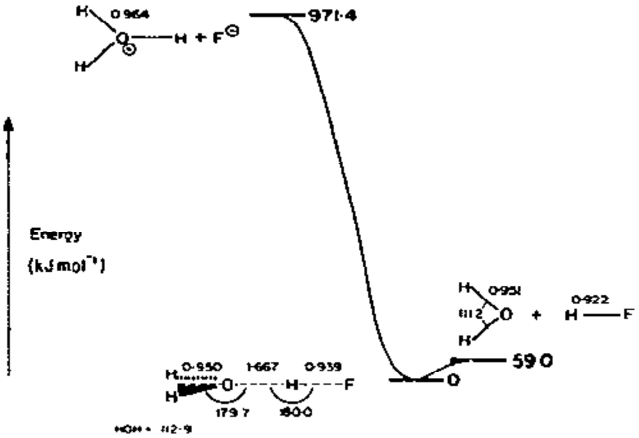


Figure 4. 4-31G optimised structures and relative energies for $H_2O \cdots H \cdots F$ systems. Bond lengths and angles are in Å and degrees. (Reproduced by permission from Chem. Phys. Lett., 64(1979)216).

The use of gaseous HBr as a working fluid for a one-step thermochemical solar energy device has been considered.[135] When Br_2 dissociation into Br$^{\cdot}$at 1500-2000K is taken into account, this system appears attractive on account of the ready separation of H_2 by effusion from Br_2 at these temperatures. Marcus has re-examined the vapour pressure and activity coefficient data for aqueous HBr.[136] He has estimated the degree of dissociation to be 0.7 in the azeotropic acid and as low as 0.3 in nearly saturated acid, 20 mol kg^{-1}. Laser flash photolysis-resonance fluorescence has been used to study the kinetics of reaction (20).[137] The rate constant $(1.19 \pm 0.14) \times 10^{-11}$ cm^3 mol^{-1} s^{-1} is independent of temperature over the range 249-416K.

$$^{\cdot}OH + HBr \longrightarrow H_2O + Br^{\cdot} \qquad \ldots(20)$$

7.2 HYDROGEN

Equilibria of the type shown in equation (21), X = N_2, CO or O_2,

$$(X)_{n-1}H^+ \quad + \quad X \quad \rightleftharpoons \quad (X)_nH^+ \qquad \ldots(21)$$

have been measured with a pulsed electron beam high ion source mass spectrometer.[138] Equilibria up to n = 7 could be observed. While the proton affinities increase in the sequence $O_2 < N_2 < CO$, the stabilities of $(X)_2H^+$ with respect to $(X)H^+$ and X increase in the reverse order. Molecular orbital calculations for $(CO)H^+$ and $(N_2)H^+$ indicate that these ions are linear, whilst $(O_2)H^+$, a triplet species, is bent. Hydrogen is generated from water by the photochemical reduction of methylviologen, MV^{2+}, and the catalytic electron transfer from reduced $MV^{\cdot +}$ to H^+ in neutral solution. Kawai et al.[139] have proposed the use of a zinc tetraphenylporphine photoelectrode for the reduction of water to H_2. The process of H_2 evolution from water containing ClO_4^- and Ce^{3+} under U.V. irradiation has been shown to involve mainly reactions (22) and (23).[140] The U.V. irradiation of aqueous solutions of Rh(III) bipyridyls, such as $[Rh(bipy)_2Cl_2]Cl$, in the presence of an electron donor, e.g. triethanolamine, leads to the evolution of H_2 gas.[141] Evidence for the involvement of Rh(I) complexes as intermediates was also discussed. Under the optimum conditions, pH 8.5 ± 0.5, the 302 nm quantum yield was found to be 0.02. Kawai and Sakata[142] have investigated the catalytic photolysis of water in the presence of active carbon and a TiO_2-RuO_2 catalyst: H_2, CO and CO_2 are produced, the content of CO_2 increasing with increasing reaction rate along with the temperature from ambient up to 80°C.

$$2Ce^{3+} \quad + \quad 2H_2O \xrightarrow{h\nu} 2Ce^{4+} \quad + \quad H_2 \quad + \quad 2OH^- \qquad \ldots(22)$$

$$Ce^{4+} \quad + \quad 4OH^- \longrightarrow CeO_2 \quad + \quad 2H_2O \qquad \ldots(23)$$

A simple H_2-air fuel cell has been developed, the H_2 for which is obtained by cracking NH_3.[143] No Pt group metal catalysts are used in the electrodes and the system contains neither a pump nor a fan. The inexpensive and reliable system has an average service life of *ca.* 3 months at 50 mA cm^{-2}.

Molecular hydrogen displaces both dinitrogen ligands in $Mo(N_2)_2L_2$, where L is a bidentate tertiary phosphine ligand.[144] The reaction product was shown to be the tetrahydride by means of ^1H and ^{31}P n.m.r, studies. Earlier observations of hydrogen exchange between $LiBH_4$ and $LiBD_4$ in etheral solution have been confirmed.[145] The ^1H n.m.r. spectra of the sodium and potassium salt mixtures in 18-crown-6 ether/chloroform solution were simplified by broad band ^2D decoupling. A successful theoretical correlation has been made of experimental data on M-H bond stretching modes of μ_2-bridged metal hydrides with the M-H-M interbond angle, θ.[146] The treatment implies that the ratio ν_{as}/ν_s of the antisymmetric to the symmetric stretching vibrations shows a linear dependence on $\tan(\theta/2)$; an empirical correlation between ν_{as} and $\sin(\theta/2)$ was found to be in even better agreement with the experimental data. A neutron diffraction study of $(Ph_3P)_2N^+[(CO)_5CrDCr(CO)_5]^-$ at 17K has been carried out to examine the nature of the Cr-D-Cr bridge.[147] The authors concluded that the bridging deuterium atom is disordered being distributed over four equivalent sites within a plane normal to the Cr-Cr axis. The limitations associated with the application of diffraction methods to such problems were thus highlighted. The structure of $(Ph_3P)_2N^+[HCo_6(CO)_{15}]^-$ has been determined by single crystal neutron diffraction analysis.[148] The anion comprises an octahedral Co_6 cluster with the proton at its centre; the average Co-H distance is 1.82Å. The proton chemical shift is anomalous, $\delta = 23.2$ p.p.m., whereas most transition metal hydrides show resonances in the high field range 0 to -40 p.p.m.

Estimates of the H-bond energies for the stepwise formation of ammonia clusters, $(NH_3)_n$, have been obtained in a molecular beam, mass spectrometric study.[149] These estimates, -4.61, -3.88, -5.22, and 3.84 ± 0.5 kcal mol^{-1} for $n = 2$ to 5 respectively indicate that the tetramer is favoured in some way. The rate constants of the gas phase proton transfer reactions of the hydronium ion at 298K (with CH_2O, MeCHO, Me_2CO, HCO_2H, $MeCO_2H$, HCO_2Me, MeOH, EtOH, Me_2O and ketene), have been measured with the flowing afterglow technique.[150a] The rate constants were compared with the various predictions for ion-molecule collisions. Bohme et al.[150b] have similarly investigated the kinetics of reaction of $H_3O^+.(H_2O)_n$, n = 1-3, with a range of bases at 298K. Their results for H_2S indicate a marked decrease (by a factor of 10^3) in rate constant for reactions (25) and (26) compared with (24), which reflects the previously reported standard free energy changes

−3.8, +7.1 and +6.3 kcal mol^{-1} for reactions (24), (25) and (26) respectively. For H_2CO the authors obtained data which suggest

$$H_3O^+ + H_2S \rightleftharpoons H_3S^+ + H_2O \qquad ...(24)$$

$$H_3O^+.H_2O + H_2S \rightleftharpoons H_3S^+.H_2O + H_2O \qquad ...(25)$$

$$H_3O^+.(H_2O)_2 + H_2S \rightleftharpoons H_3S^+.(H_2O)_2 + H_2O \qquad ...(26)$$

that the basicities of $H_3O^+.(H_2O)_3$ and $H_3CO^+.(H_2O)_3$ are comparable.

It has been shown that the hydrogen-bonding energies in $ZH^+\cdots(OH_2)_n$ decrease with increasing basicity of the substituted pyridine Z.[151] This decrease of solvation energy of the ions is largely responsible for the attenuation of the substitutent effect on the pyridine basicity in aqueous solution. In a continued study of the i.r. spectra of the ammonium ion in crystals, the NH_3D^+ ion has been used as the probe ion.[152] This paper discusses the problem of the fundamental vibrational frequencies of the 'free' ammonium ion and reviews the criteria of hydrogen bonding in ammonium halides.

Raymond et al.[153] have obtained the tris(thiobenzohydroximato)-Cr(III) complex, $Na_2(Et_3MeN)[Cr(PhC(S)=N(O))_3].\frac{1}{2}NaH_3O_2.18H_2O$, and determined its structure by X-ray methods. The $H_3O_2^-$ anion present in the lattice has not been characterised previously and is of great interest on account of the short O-H···O distance, 2.29(2)Å, which is comparable with that in the isoelectronic HF_2^- ion. Figure 5 shows a perspective view of the hydrated hydroxide ion and its interactions with neighbouring water molecules. The energy of the $O_2NOHONO_2^-$ ion as a function of the two torsional angles (around the OHO vector and around the O-NO_2 axis) have been calculated by ab initio schemes.[154] The energy of the planar conformation is a minimum for OHO = 2.35Å. A single crystal neutron diffraction study of $[Rhpy_4Cl_2]H(NO_3)_2$ at 298K has demonstrated that the anions $(O_2NOHONO_2)$ are symmetric but orientationally disordered.[155] Contrary to earlier X-ray findings the hydrogen bond within this anion is very short (O-H-O = 2.46(2)Å). Catti et al.[156] have reported that the sulphate groups in the $(O_3SOHOSO_3)^{3-}$ anion, in the trisodium salt, are bonded through a very short hydrogen bond (O-H-O = 2.434(4)Å). A strong and linear correlation between the lengths of S-O(H) and O-H-O bonds in 19 other hydrogen sulphate derivatives was established on the

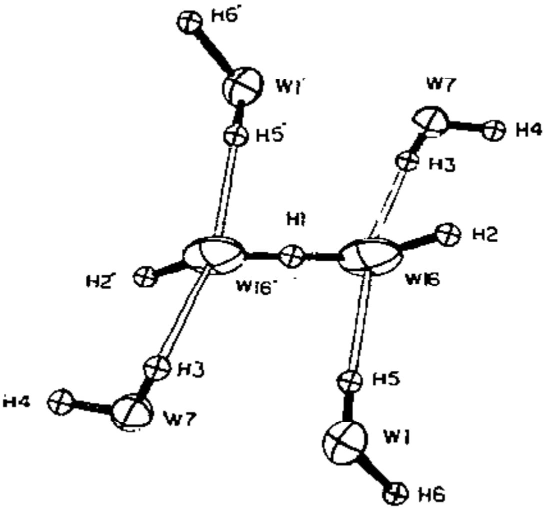
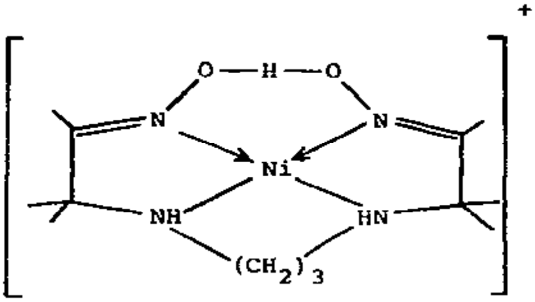


Figure 5. A perspective view of the structure of the $H_3O_2^-$ anion and the weak hydrogen bonding formed between it and adjacent waters of crystallisation. Hydrogen atoms 2,3,4 and 6 have been located from the difference Fourier. Hydrogen atoms 1 and 5 were not seen in the electron density maps. Their positions are deduced from those of the other atoms in the structure. (Reproduced by permission from J. Am. Chem. Soc., 101(1979)3688).

basis of other published structures.

The usefulness of ^1H, ^2H, and ^3H n.m.r. isotope effects as a means of studying the shape of the potential energy surface of hydrogen bonded systems has been discussed by Altman and coworkers.[157] A combined room-temperature neutron and X-ray diffraction study of hydrated 2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone-oximato)nickel(II) chloride has been performed to investigate the influence of the steric requirements of the ligand and the size of the metal ion on the short intramolecular O-H-O bond. The complex cation (9) has square planar coordination about the nickel atom: the short intramolecular hydrogen bond (O···O = 2.409(10)Å) has an angle at hydrogen of 170(1)° and the O-H distances are nearly equal, 1.16(2) and 1.26(2)Å. The crystal structure at -150°C of



(9)

the rhombohedral form of methylammonium fluoride, $MeNH_3F$, shows that fluorine is hydrogen bonded to the cation with F···H 1.73Å, F(H)N 2.66Å and the angle FHN = 165°.[159] The structure of crystalline trifluoroacetic acid at 83K confirms that centrosymmetric, hydrogen bonded dimers are present, O-H···O 2.648(3)Å.[160] The correlations between bond lengths and angle at a donor oxygen atom and the H-bonded parameter, C-O versus O-H and C-O-H versus O-H, have been derived for H-bonded carboxyl groups using accurate neutron diffraction data.[161] The C-O distance decreases linearly with increasing O-H distance but the C-O-H angle shows a poor correlation with scatter over several degrees.

Mateescu and Benedikt[162] have obtained ^{17}O n.m.r. spectra of H_3O^+ from a 1.5M solution of ^{17}O-enriched water in SO_2 in the presence of $HF-SbF_5$. The undecoupled spectrum showed a 1:3:3:1 quartet, at -15°C ($J(^{17}O-H)$ = 106Hz) downfield from external H_2O, which collapsed to a singlet when proton decoupled. The same workers also presented evidence for the formation of protonated acetone under similar conditions.

The He(I) photoelectron spectra of the gaseous H-bonded complexes $R_3CO_2H-MeEt_2N$, $R_3CO_2H-nPr_3N$, R = CF_3 or C_2F_5, have been observed.[163] It was found that the non-bonding orbital of the proton acceptor is stabilised significantly while the three upper occupied orbitals of the proton donor are destabilised. The syntheses of $H_3O_2^+$ salts, with $Sb_2F_{11}^-$, SbF_6^- and AsF_6^-, have been achieved in anhydrous HF by Christe et al..[164] They were shown to be metastable solids which decomposed to the corresponding H_3O^+ salts and O_2 in the temperature range +20 to 50°C. The electrical conductivity of crystalline dodecamolybdophosphoric acid, $H_3Mo_{12}PO_{40}\cdot 29H_2O$, and the analogous tungstic acid have been measured.[165] High conductivities of 0.18 and 0.17 $\Omega^{-1}cm^{-1}$ at 25°C and low activation energies, 15.5 and 13.7 kJ mol^{-1}, were obtained.

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