

Chapter 7

THE HALOGENS AND HYDROGEN

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7.1 HALOGENS

7.1.1 The Elements

Rose and Marier¹ 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



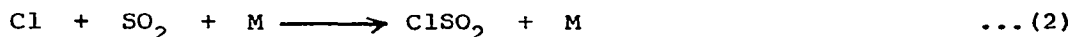
223 to 293K and in the presence of Ar has been measured by e.s.r. spectroscopy.² The results are consistent with

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

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 $\text{CF}_3\text{S}_2\text{CF}_3$ 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 , $\text{CCl}_2\text{FCClF}_2$, CH_3CCl_3 , CCl_4 , CHCl=CCl_2 , and $\text{CCl}_2=\text{CCl}_2$ 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 $2 \times 10^{-10}\text{v/v}$ then Strattan et al.⁷ have suggested that reaction (2) ($\text{M} = \text{Ar}, \text{N}_2$



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	$\text{CCl}_2\text{F}-\text{CClF}_2$	CH_3-CCl_3	CCl_4	CHCl_3	$\text{CCl}_2=\text{CCl}_2$
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 Forsén¹¹ 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 $\text{I}(5p^4 6s, ^2P_{3/2})$ 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 $((\text{CHI}_x)_n)$ 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 , $\text{P} \cdot 4\text{I}_2$, 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 $\sigma(300\text{K})$ value for these crystals is $40\Omega^{-1}\text{cm}^{-1}$. Manometric measurements in the range 40° to 140°C 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 $+16.8 \text{ JK}^{-1}\text{mol}^{-1}$ for the o-tolidine complex to $-21.0 \text{ JK}^{-1}\text{mol}^{-1}$ 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 Woolf²³ 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 hexahalosmate(IV) anions, such as trans- $[\text{OsFCl}_4\text{I}]^-$, have been prepared by Shukla and Preetz from the ion-pair reaction between trilaurylammonium fluoride, $(\text{TLAH})\text{F}$, and $(\text{TLAH})_2[\text{OsCl}_5\text{I}]$ 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 $\text{Bu}_4\text{NF} \cdot 2\text{oxime}$, 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 $\text{KF} \cdot 2\text{H}_2\text{O}$ 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 Radom³², however, argue on the basis of an ab initio M.O. study that "the $\text{H} \cdots \text{F}$ bond in the carboxylic acid-fluoride system should not be considered a hydrogen bond." They prefer to describe the $\text{HCO}_2\text{H} \cdots \text{F}^-$ 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

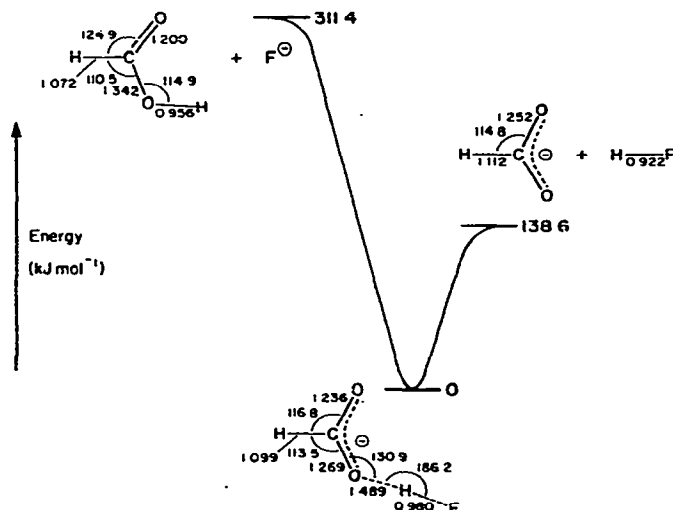
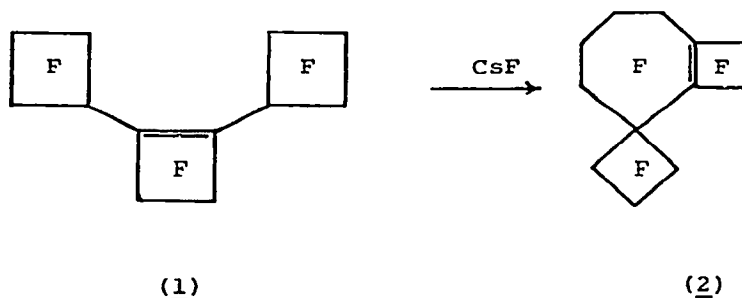


Figure 1. 4-31G optimised structures and relative energies for $[\text{HCOO} \cdots \text{H} \cdots \text{F}]^-$ systems. Bond lengths and angles in Å and degrees (reproduced by permission from Chem. Phys. Lett., 64 (1979) 216).

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

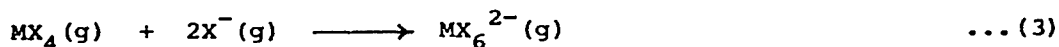
The results of an investigation of the isothermal (25°C) solubility in the KF-DMSO-MeCO₂H system show that the solubility of KF increases with increasing acetic acid concentration:³³ the solvated products were shown to be KF.MeCO₂H and KF.2MeCO₂H. Solvated alkaline earth difluorides MF₂·2HCO₂H, M = Sr 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 coworkers³⁵ 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.



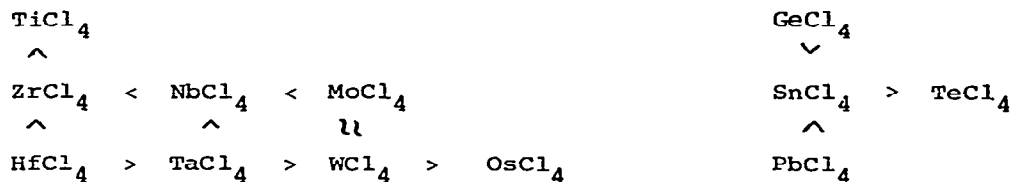
Ion cyclotron resonance techniques have been used to examine the formation and reaction of negative ions derived from WF₆.³⁶ Electron transfer reactions are consistent with a value of 3.5 ± 0.1 eV for the electron affinity of WF₆. Fluoride ion transfer reactions suggest the sequence of bond dissociation energies with the value

$$D(\text{SiF}_4\text{-F}^-) < D(\text{WF}_6\text{-F}^-) < D(\text{BF}_3\text{-F}^-)$$

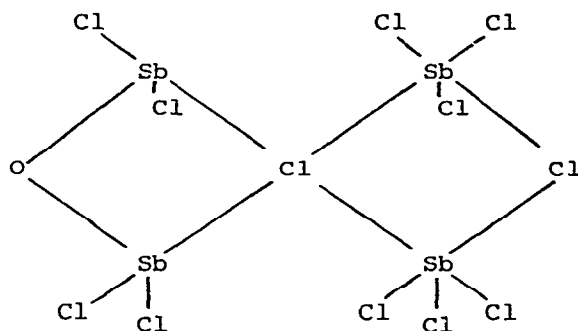
for $D(\text{WF}_6\text{-F}^-) = 69 \pm 5 \text{ kcal mol}^{-1}$. Double halide ion affinities corresponding to reaction (3) have been calculated from lattice



energy studies for a wide range of elements.³⁷ Acceptor powers towards Cl⁻ are as follows:



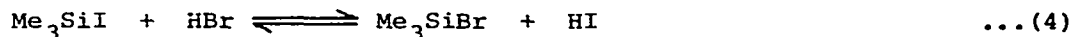
The product of the photolytic reaction between SbCl_3 and ferrocene in benzene, in the presence of O_2 , has been characterised by X-ray crystallography and shown to contain an octameric unit, $[\text{Sb}_4\text{Cl}_{12}\text{O}]_2^{4-}$.³⁸ This anion is unusual on several accounts and especially because of



(3)

the quadruply bridging chlorine atom in each pair of the $\text{Sb}_4\text{Cl}_{12}\text{O}$ half units (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 $D(\text{Me}_3\text{Si-I})$ was

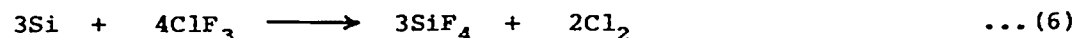


hence estimated to be 322kJ mol^{-1} .

7.1.3 Interhalogens and Related Species

The review by Shamir⁴¹ of the polyhalogen and interhalogen cations supercedes that published by Gillespie and Morton in 1971. Andrews⁴² 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 Morokuma⁴⁴ 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 $\text{C}_4\text{F}\cdot\text{ClF}_3$.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 ³⁵Cl n.q.r. spectra



of MClF_4 , $\text{M} = \text{Cs}, \text{Rb}$ 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 2.54 Å 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.

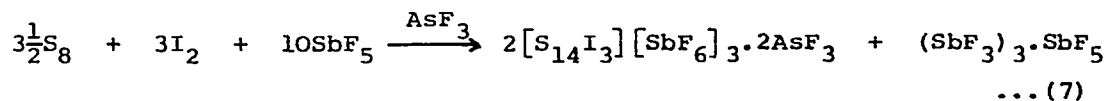
The i.r. spectra of M^+BrF_2^- ion pairs in Ar matrices has been obtained from samples of co-deposited $\text{MF}/\text{F}_2/\text{Ar}$ at 15K.⁵³ Absorptions due to symmetric FXF^- and asymmetric XFF^- were reported for both $\text{X} = \text{Br}$ and I . Sulphur dioxide is oxidised by $\text{Br}_3^+\text{MF}_6^-$, $\text{M} = \text{As}$ 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 $r_{\text{av}}(\text{Br-F}) = 1.753(2)\text{Å}$, $\Delta r_{\text{av}}(\text{BrF}_{\text{eq}} - \text{BrF}_{\text{ax}}) = 0.069(6)\text{Å}$ and $F_{\text{ax}}\text{BrF}_{\text{eq}} = 85.14(4)^\circ$.

BrF_5 and its complexes with SbF_5 , $\text{BrF}_5 \cdot n\text{SbF}_5$ $n = 1, 2, 3$ 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 .

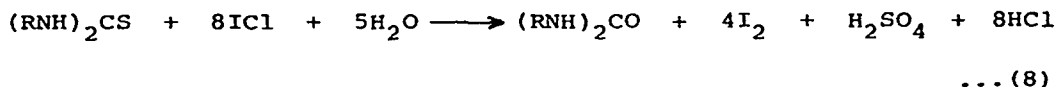
Halogens, when added to flames, usually generate negative ions. In addition iodine produces I^+ , I_2^+ , IO^+ and I^{2+} whereas bromine gives only Br^+ and Br_2^+ ; on the other hand chlorine forms no positive ions whatsoever. The dominant species are I^+ and Br^+ . Burdett and Hayhurst⁵⁸ have investigated in detail the disappearance of I^+ from the burnt gases of flames from 1820 to 2650K.

The $[\text{S}_{14}\text{I}_3]^{3+}$ ion has been produced as the SbF_6^- salt by reaction (7).⁵⁹ The X-ray structure shows that the cation comprises



two S_7I^+ cations joined by S through an I at an inversion centre such that the SI distance is 2.67\AA . 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 (2.90\AA) and shorter (2.68\AA) outer I-I bonds. Three I_5^+ units are joined by a weak (3.42\AA) 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



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 $BI^+_n I_{n-1}^-$ and the N-iododipyridinium salt, $B_2I^+_n I_{n-1}^-$. 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 acetate groups, thus raising the coordination of iodine to pentagonal planar (by O(1)-O(4) and C(5)), see Figure 2. In the bis(dichloro-

acetate) (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)

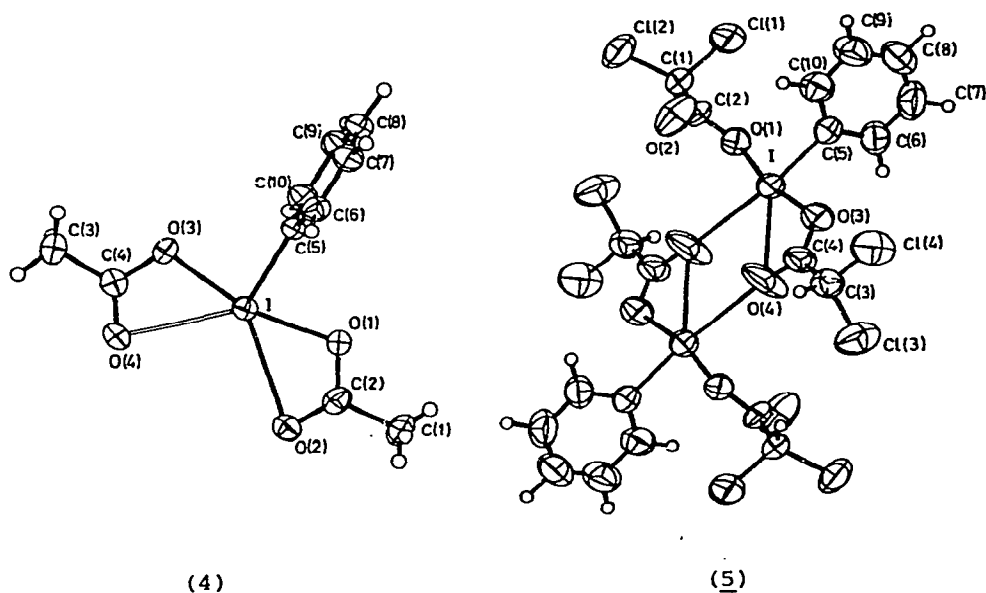
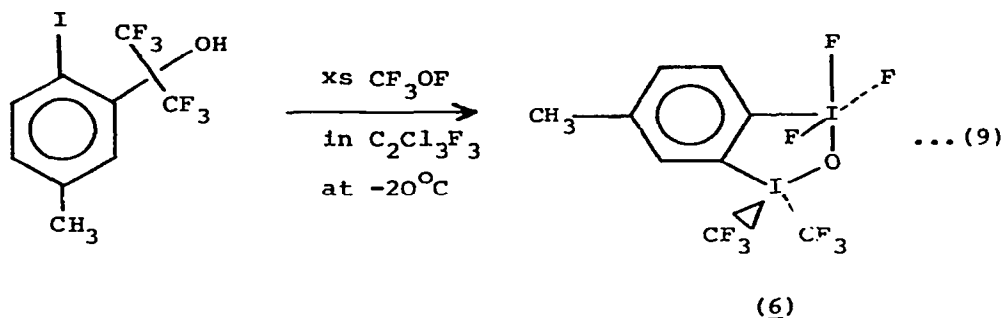


Figure 2. ORTEP views of diacetatophenyliodine(III) (4) and of bis(dichloroacetato)phenyliodine(III) (5).
(Reproduced by permission from J. Chem. Soc. Dalton Trans., (1979)854).

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



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 $r_{\text{av}}(\text{IF}) = 1.860(2)\text{\AA}$, $\Delta r_{\text{av}}(\text{IF}_{\text{eq}} - \text{IF}_{\text{ax}}) = 0.034(14)\text{\AA}$, and $F_{\text{ax}}\text{IF}_{\text{eq}} = 82.1(6)^\circ$.

7.1.4 Oxides, Oxide Halides, and Oxoanions

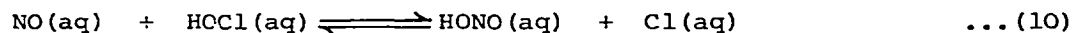
The action of F_2 on a suspension of dry sodium trifluoroacetate in a chlorofluorocarbon at -75°C produces a stable oxidising solution containing approximately 50% $\text{C}_2\text{F}_5\text{OF}$.⁶⁹ Such a mixture acts on steroidal enol acetates to give α -fluoroketones in good yields.⁷⁰ Fluorine gas reacts with trifluoroacetic acid or the hydrated sodium salt leading to the formation of trifluoroacetyl hypofluorite.⁶⁹ Mass spectra of CF_3OF , $\text{CF}_2(\text{OF})_2$, CF_3OOF , CF_3OOCF_3 and $\text{CF}_3\text{OOOCF}_3$ 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 $[\text{Cr}(\text{NH}_3)_5\text{N}_3]^{2+}$ lead to transfer of oxygen with formation of HOO^*F , $\text{O}_3\text{SOO}^*\text{H}$, and $[\text{Cr}(\text{NH}_3)_5\text{NO}^*]^{2+}$ 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 iso-electronic 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 SCF angle are $1.412(10)\text{\AA}$ 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°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 ≤ 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



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

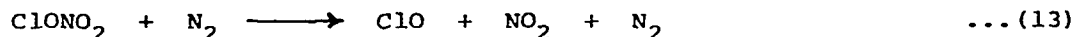


offer a promising explanation of reducing NO and NO_2 emissions from industrial plants.

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



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 of reaction (13) have been studied by infrared



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

Katsuhara and DesMarteau⁸² report that chlorine(I) triflate, $\text{ClOSO}_2\text{CF}_3$, adds stereospecifically to the isomers of $\text{CFH}=\text{CFH}$ and that the displacement of chlorine from the product $\text{CF}_3\text{SO}_3\text{CFH.CFHCl}$ 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 - $\text{CF}_3\text{CO}_2\text{Cl}$, $\text{C}_2\text{F}_5\text{CO}_2\text{Cl}$, $\text{C}_3\text{F}_7\text{CO}_2\text{Cl}$, $\text{HCF}_2\text{CO}_2\text{Cl}$, and $\text{ClCF}_2\text{CO}_2\text{Cl}$ - which have been characterised by i.r., n.m.r., and Raman spectroscopy.⁸³ $\text{CF}_2(\text{CF}_2\text{CO}_2\text{Cl})_2$ 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 $^2\Sigma^- + ^2\Pi_1$; 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



Evidence was also obtained for the formation of a ClOOC1 dimer whose

stability at 298K is kinetically significant. The low intensity photolysis of $\text{Cl}_2 + \text{O}_2 + \text{N}_2$ 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} .

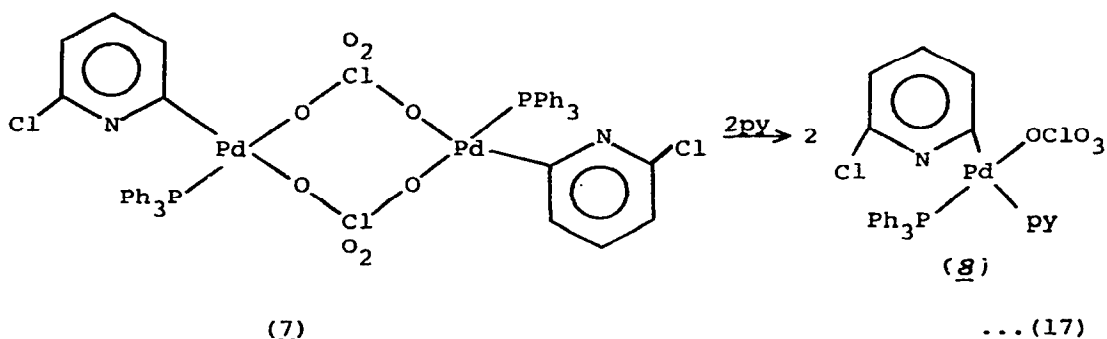
An investigation of the thermal decomposition of AgClO_3 indicates that part of the salt is oxidised to AgClO_4 and that the final product is AgCl .⁸⁹ Chlorate ion can be determined quantitatively by reduction with Cl^- in H_2SO_4 to form Cl_2 ;⁹⁰ the latter reacts cleanly with methyl orange and the 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, $-22.6 \pm 1.0\text{kJ mol}^{-1}$, 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 $\text{enH}^+\text{ClO}_4^-$ and $\text{HN}=\text{CHCH}_2\text{NH}_3^+\text{ClO}_3^-$.⁹² Schilt⁹³ 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 $\text{Li}_2\text{Al}(\text{ClO}_4)_5$ 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 $\text{MAl}(\text{ClO}_4)_4 \cdot \text{HClO}_4$, $\text{M} = \text{NH}_4$, Rb or Cs , $\text{Rb}_2\text{Al}(\text{ClO}_4)_5$ and $\text{Cs}_2\text{Al}(\text{ClO}_4)_5 \cdot \text{HClO}_4$ towards HClO_4 have also been reported.⁹⁶

The effect of hydration on the ion pairs $\text{Li}^+\text{ClO}_4^-$ 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 $[\text{Pd}(\text{ClO}_4)(\text{C}_5\text{H}_3\text{NCl})(\text{PPh}_3)]_2$, (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.



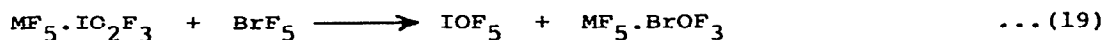
The rate constant for reaction (18) has been measured:⁹⁹ it obeys



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 . Tevault¹⁰¹ 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 $\text{S}_2\text{O}_3^{2-}$ 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 $[\text{OH}^-]^{-1}$ -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), $\text{M} = \text{As}$ or Sb . The Raman and ^{19}F n.m.r. spectra of these adducts were



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 $\text{BrF}_2^+\text{SbF}_6^-$ 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 $\text{PhI}(\text{NO}_3)_2$. 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

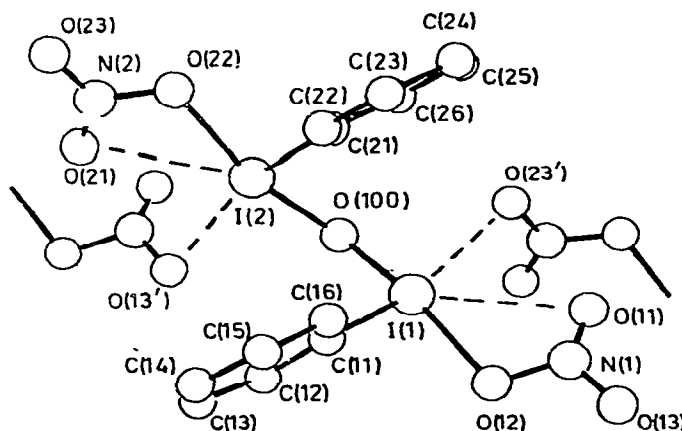


Figure 3. A view of the molecule μ -oxo-bis[nitrato(phenyl)iodine(III)] showing the I---O secondary interactions. (Reproduced by permission from J. Chem. Soc. Dalton Trans., (1979)851).

the reactions can be followed potentiometrically.¹⁰⁶ The standard enthalpy of formation of CsIO_3 has been redetermined calorimetrically.¹⁰⁷ The result, $-125.39 \pm 0.47 \text{ kcal mol}^{-1}$, 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 $520\text{--}560^\circ\text{C}$.¹⁰⁸ In the vicinity of the melting point the activation energy of the decomposition is 56 kcal mol^{-1} . Solubility in the $\text{Al}(\text{IO}_3)_3\text{--LiIO}_3\text{--HIO}_3\text{--H}_2\text{O}$ system at 25°C has been investigated. The crystallization fields of HIO_3 , $\alpha\text{-LiIO}_3$, $\text{Al}(\text{IO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{IO}_3)_3 \cdot 2\text{HIO}_3 \cdot 6\text{H}_2\text{O}$ and the solid solution of HIO_3 and LiIO_3 have been determined.¹⁰⁹ The new phase $2\text{KIO}_3 \cdot \text{Mn}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$, similar to the analogous $\text{Zn}(\text{II})$ and $\text{Co}(\text{II})$ phases, has been observed in the $\text{KIO}_3\text{--MnIO}_3\text{--H}_2\text{O}$ system at 50°C .¹¹⁰ The crystal structure of triclinic $\text{Al}(\text{IO}_3)_3 \cdot 8\text{H}_2\text{O}$ 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 Tabatabai¹¹³ have resolved the absorption into two overlapping Gaussian bands at 222nm ($\epsilon_{\text{max}} 1000 \text{ m}^2 \text{mol}^{-1}$) and 280nm ($\epsilon_{\text{max}} 27 \text{ m}^2 \text{mol}^{-1}$). 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 Stevens¹¹⁵ 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 $\text{NF}_4^+ \text{IO}_2\text{F}_4^-$. Two volatile iodine-containing species were produced in the ratio 2:1 which were characterised as the cis- and trans-isomers of $\text{OI}(\text{OF})\text{F}_4$. 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, $\text{ROH} \cdots \text{HF}$, for which the vibration wavenumbers $\bar{\nu}(\text{F-H})$ 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 Klein¹¹⁹ 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.

Gut¹²⁰ 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 .

Faris¹²⁴ 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 $0 - 80^\circ\text{C}$.¹²⁵ The redox properties of M^{n+}/M or $\text{M}^{n+}/\text{M}(\text{Hg})$ couples have been investigated in 0 - 60 wt.% HF for $\text{M} = \text{Cd}^{2+}$, 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 $25.5 \pm 1.0 \text{ kJ mol}^{-1}$ 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 0.998 Å respectively. In the $\text{NH}_4\text{F-HF-DMSO}$ 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 $\text{NH}_4\text{PF}_6\text{-HF-DMSO}$ 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 $1377.0(965.5) \text{ cm}^{-1}$ 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 $\text{Cl}^-\cdots\text{HCCl}_2$ anion as the product of electron capture by CHCl_3 . Under the same conditions^{131b} CHF_3 , CHF_2Cl and CHF_2Br generate both $\text{F-H}\cdots(\text{CFX})^-$ and $\text{X-H}\cdots(\text{CF}_2)^-$, $\text{X} = \text{F}, \text{Cl}$ or Br , whereas CHF_2I produces $\text{F-H}\cdots(\text{CFI})^-$ and $\text{I}^-\cdots(\text{HCF}_2)$. Bouma and Radom³² have carried out ab initio MO calculations on $\text{H}_3\text{O}^+\text{F}^-$, $\text{H}_2\text{O}\cdots\text{H}\cdots\text{F}$ and $\text{H}_2\text{O}\cdots\text{HF}$; their results are depicted in Figure 4.

The ^1H n.m.r. spectra of mixtures of ROH ($\text{R} = \text{H}, \text{Me}, \text{Et}$) or HBr in $\text{CF}_2\text{Br}_2\text{-CD}_2\text{Cl}_2$ 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 $\text{Me}_2\text{SO}\cdot 2\text{HF}$ 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 $\leq 3\text{M}$ Me_4NCl , which the ion pairs of Me_3NHCl are apparently solvated by 5 HCl molecules.

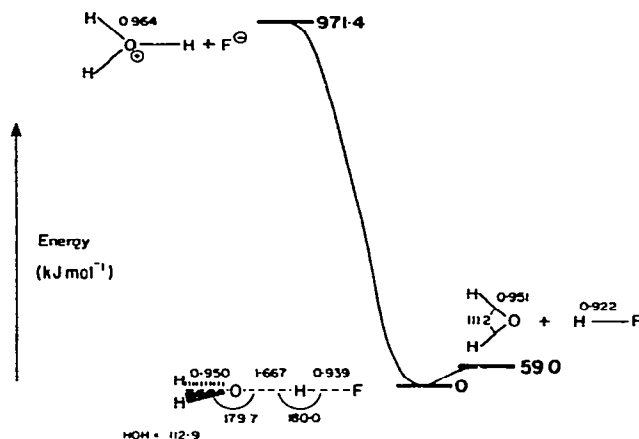


Figure 4. 4-31G optimised structures and relative energies for $\text{H}_2\text{O} \cdots \text{H} \cdots \text{F}$ systems. Bond lengths and angles are in \AA and degrees. (Reproduced by permission from Chem. Phys. Lett., 64(1979)216).

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^* 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 $(1.19 \pm 0.14) \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is independent of temperature over the range 249–416K.

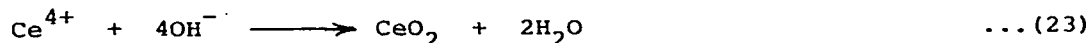
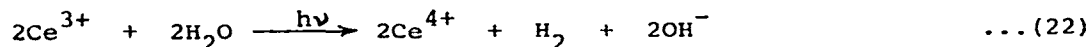


7.2 HYDROGEN

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



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 Sakata¹⁴² 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 $80^\circ C$.

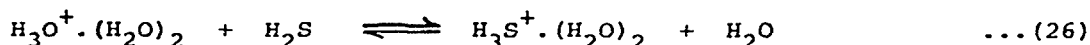
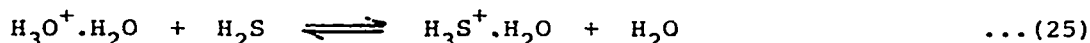
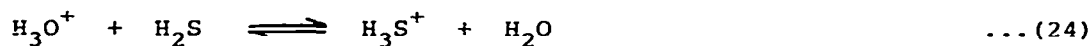
A simple H_2 -air fuel cell has been developed, the H_2 for which is obtained by cracking NH_3 .¹⁴³ No Pt group metal catalysts are used in the electrodes and the system contains neither a pump nor a fan. The inexpensive and reliable system has an average service life of ca. 3 months at 50 mA cm^{-2}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

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 $v_{\text{as}}/v_{\text{s}}$ of the antisymmetric to the symmetric stretching vibrations shows a linear dependence on $\tan(\theta/2)$; an empirical correlation between v_{as} and $\sin(\theta/2)$ was found to be in even better agreement with the experimental data. A neutron diffraction study of $(\text{Ph}_3\text{P})_2\text{N}^+[(\text{CO})_5\text{CrDCr}(\text{CO})_5]^-$ 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 $(\text{Ph}_3\text{P})_2\text{N}^+[\text{HCo}_6(\text{CO})_{15}]^-$ 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 1.82\AA . 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, $(\text{NH}_3)_n$, 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 $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$, $n = 1-3$, 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

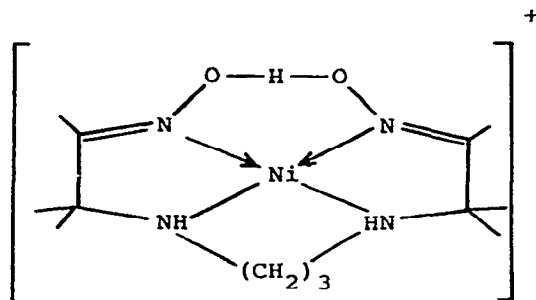
-3.8, +7.1 and +6.3 kcal mol⁻¹ for reactions (24), (25) and (26) respectively. For H₂CO the authors obtained data which suggest



that the basicities of H₃O⁺.(H₂O)₃ and H₃CO⁺.(H₂O)₃ are comparable.

It has been shown that the hydrogen-bonding energies in ZH⁺... (OH₂)_n decrease with increasing basicity of the substituted pyridine Z.^{151,2} This decrease of solvation energy of the ions is largely responsible for the attenuation of the substituent effect on the pyridine basicity in aqueous solution. In a continued study of the i.r. spectra of the ammonium ion in crystals, the NH₃D⁺ 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, Na₂(Et₃MeN)[Cr(PhC(S)=N(O))₃]. $\frac{1}{2}$ NaH₃O₂.18H₂O, and determined its structure by X-ray methods. The H₃O₂⁻ 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 HF₂⁻ ion. Figure 5 shows a perspective view of the hydrated hydroxide ion and its interactions with neighbouring water molecules. The energy of the O₂NOHONO₂⁻ ion as a function of the two torsional angles (around the OHO vector and around the O-NO₂ 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 [Rhpy₄Cl₂]H(NO₃)₂ at 298K has demonstrated that the anions (O₂NOHONO₂) 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 (O₃SOHOSO₃)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



the rhombohedral form of methylammonium fluoride, MeNH_3F , shows that fluorine is hydrogen bonded to the cation with $\text{F}\cdots\text{H}$ 1.73\AA , $\text{F}(\text{H})\text{N}$ 2.66\AA and the angle $\text{FHN} = 165^\circ$.¹⁵⁹ The structure of crystalline trifluoroacetic acid at 83K confirms that centrosymmetric, hydrogen bonded dimers are present, $\text{O}-\text{H}\cdots\text{O}$ $2.648(3)\text{\AA}$.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 Benedikt¹⁶² 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 $\text{HF}-\text{SbF}_5$. The uncoupled spectrum showed a 1:3:3:1 quartet, at -15°C ($J(^{17}\text{O}-\text{H}) = 106\text{Hz}$) 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 $\text{He}(\text{I})$ photoelectron spectra of the gaseous H-bonded complexes $\text{R}_3\text{CO}_2\text{H}-\text{MeEt}_2\text{N}$, $\text{R}_3\text{CO}_2\text{H}-n\text{Pr}_3\text{N}$, $\text{R} = \text{CF}_3$ 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 $\text{Sb}_2\text{F}_{11}^-$, 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, $\text{H}_3\text{Mo}_{12}\text{P}_{40}\text{O}_{165}\cdot 29\text{H}_2\text{O}$, and the analogous tungstic acid have been measured. High conductivities of 0.18 and 0.17 $\Omega^{-1}\text{cm}^{-1}$ at 25°C and low activation energies, 15.5 and 13.7 kJ mol^{-1} , were obtained.

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