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Plasmo-chemical Reactions of Fluorine and Fluorides

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The reactions of fluorine and its compounds under plasma conditions are discussed. 145 References.

CONTENTS

I.	Introduction	31
II.	Synthesis of the nitrogen fluorides, trifluoramine oxide, and tetrafluoro-ammonium salts	32
III.	Synthesis of oxygen fluorides	34
IV.	Synthesis of the halogen fluorides and of chlorine oxytrifluoride	34
V.	Synthesis of the inert gas fluorides	35
VI.	Other reactions of fluorine and fluorides	36

I. INTRODUCTION

In spite of the very high reactivity of fluorine, reactions involving this element often need to be activated by an electrical discharge or by u.v. radiation. Interest in the reactions of fluorine in discharges was stimulated by recent developments in the synthesis of fine inorganic chemicals, and by the search for new oxidisers and high-energy compounds. The plasmo-chemical synthesis of fluorides is often either the only available method or the most attractive one.

Atomic fluorine, formed by passing molecular fluorine through an electrodeless h.f. discharge (40 MHz, 50 W), has been detected[1] by ESR. A dark red glow discharge, whose spectrum contains strong optical lines from neutral fluorine atoms, develops in a fast flow of the gas at a few hundred Pascal pressure.

Small quantities of atomic fluorine in electrical discharges are usually prepared by using a mixture of fluorine (or volatile fluoride) with an inert gas. For example, the following mixtures have been used: fluorine and argon (0.1–20% F_2),[2-9] fluorine and helium (1–20%),[7,9,10] sulphur hexafluoride and helium[11,12]; atomic fluorine has also been prepared from carbon tetrafluoride[4,13-15]. Power is supplied to the gas reactor from a low-power h.f. or microwave generator, for example a standard microwave generator of frequency 2450 MHz and <200 W output power. The discharge tubes are made of quartz or alumina: the latter is more stable towards atomic fluorine[3-8], but it produces dielectric losses higher than those of quartz tubes. The gas flow emerging from the reactor is used to study the reactions of atomic fluorine (see Ref.16 for a comprehensive review).

The dissociation of fluorine in a microwave discharge can be as high as 60–90%[3,9,10], but the concentration of atomic fluorine in the outlet gas decreases rapidly as a result of recombination and reaction with the wall of the apparatus. The recombination rate constant ($F + F + Ar \rightarrow F_2 + Ar$) is estimated[17] to be $(1.8–6.0) \times 10^{13}$ cm^6 mole^{-2} s^{-1}. A study of the recombination of fluorine atoms in the presence of argon at 295 K and 10–81 mmHg pressure gave an experimental value of $(2.9 \pm 0.2) \times 10^{13}$ cm^6 mole^{-2} s^{-1} for the constant[8]. This value is two orders of magnitude lower than the corresponding rate constants for the recombination of Cl, Br, I, O, and H atoms in argon. Molecular nitrogen (as the third body) is approximately 10 times more effective than argon in bringing about the homogeneous recombination of atomic fluorine[8].

A significant proportion of the fluorine atoms is lost on the apparatus walls. On a quartz surface the loss of F atoms occurs mainly by the reaction with SiO_2, accompanied by the formation of silicon tetrafluoride[4,18,19] and of fluorosiloxane polymers[20]. The probability of disappearance of F atoms as a result of wall collisions has been determined[19,21] for the following surfaces: glass, quartz, mullite–silica, Teflon, copper, stainless steel, nickel, aluminium alloys, and gold.

The formation of fluorine atoms from F_2 molecules in an electrical discharge can take place by different mechanisms: the most probable are described by Eqns.(1) and (2):

$$F_2 + e \rightarrow (F_2^-)^* \rightarrow F + F + e \,, \qquad (1)$$

$$F_2 + e \rightarrow (F_2^-)^* \rightarrow F + F^- \,. \qquad (2)$$

The minimum energy of the colliding electron needed for reaction (1) is 1.5 eV; the dissociative attachment reaction (2) is exothermic, and does not require an activation energy[22]. Reactions (3), (4), and (5)

$$F_2 + e \rightarrow F_2^+ + 2e \qquad (3)$$

$$F_2 + e \rightarrow F^+ + F + 2e \qquad (4)$$

$$F_2 + e \rightarrow F^+ + F^- + e \qquad (5)$$

can take place if the energy of the colliding electrons is not less than 16.6, 19.0, and 15.4 eV respectively[22]. The cross-section of reaction (5) increases monotonically with the electron energy from ~16 to 32 eV: this reaction is predominant for field strengths of ~10^4 V cm^{-1}.[23,24]. The presence of F_2^+ ions in gaseous fluorine passed through a glow discharge (50 mA, 15 kV) has been demonstrated[25] spectroscopically. The reaction $F_2^+ + F^- \rightarrow F + F + F$ is thought to be another probable path for the formation of F atoms[22].

The number of F atoms generated by collisions with electrons is proportional to the energy of the electron beam[22]. The rate of dissociation of F_2 molecules in a glow discharge at 0.5 mmHg pressure increases linearly from 3×10^{16} to 1.2×10^{17} cm^{-3} s^{-1} as the current increases from 4 to 45 mA.[26] The dissociative attachment of electrons to the F_2 molecule has been shown[27,28] to be one of the basic rate-limiting processes in the dissociation of fluorine in the positive column of a glow discharge for currents in the range 0.5–50 mA. The thermal dissociation of fluorine molecules in gas discharge plasmas can be ignored because of the relatively low "molecular" temperature of the plasma[27,29].

From sulphur hexafluoride in a discharge the F atoms are formed mainly by the reaction $SF_6 \rightarrow SF_5 + F$;[30] the dissociation of CF_4 gives not only fluorine atoms and molecules, but also C_2F_6, CF_2, and other fluorinated compounds[4]. Thus, in

spite of their ready availability in a very pure form, SF_6 and CF_4 are not the most convenient sources of fluorine for chemical synthesis in electrical discharges.

Low-frequency glow discharges are used most frequently for the synthesis of fluorides: reactions in electrodeless h.f. and microwave discharges, or in silent (barrier) discharges, have not been studied in detail. Whenever possible, the prepared mixture of fluorine (or volatile fluoride) and the other reactant is introduced into the discharge reactor, or the reactants are condensed on the reactor wall and exposed to fluorine (or a fluoride) which has been activated in the discharge. Reactions involving fluorine or a fluoride are usually carried out in reactors cooled to very low temperatures. Often a valuable product can be synthesised only if the reactor walls are cooled in liquid nitrogen, but this is easily done because the discharge current is usually 20–50 mA, corresponding to a power dissipation of only 100–150 W.

In the following Sections we shall review experimental data on the reactions of fluorine and fluorides in an electrical discharge reported since 1969–1970, and therefore not included in earlier reviews[31,32]. Some older work not mentioned in those reviews will also be discussed here.

II. SYNTHESIS OF THE NITROGEN FLUORIDES, TRIFLUORAMINE OXIDE, AND TETRAFLUORO-AMMONIUM SALTS

1. Synthesis of Nitrogen Trifluoride

Nitrogen fluorides have a variety of applications in the synthesis of fine inorganic chemicals and in preparative organic chemistry[33]. In the absence of external agencies such as electrical discharges or ionising radiation fluorine does not react with nitrogen. The nitrogen fluorides NF_3, N_2F_4, N_2F_2, and N_3F are therefore usually prepared from compounds containing bound nitrogen. However, the synthesis of nitrogen trifluoride from the elements is thought[34] to be thermodynamically possible at temperatures below ~900 K. A calculation[35] of the equilibrium composition of the nitrogen–fluorine system shows that at 200–1000 K, for total pressures of 20 or 760 mmHg, and for atomic ratios F : N = 1 : 3, 1 : 1, or 3 : 1 the main fluorine-nitrogen component of the system at equilibrium is nitrogen trifluoride[36], whose concentration is a maximum and close to 1 (in mole fraction) at 200–600 K. As the temperature increases to 700–1000 K the concentration of NF_3 decreases as a result of dissociation, and at 1500 K it becomes negligibly small[37].

The preparation of NF_3 in 30% yield from the elements in a glow discharge was reported[38] in 1964, but the synthesis of NF_3 in a glow discharge appears[39] to have first achieved in 1960. The synthesis of nitrogen trifluoride is possible whether or not the discharge tube is cooled in liquid nitrogen: if all other conditions are the same, a better yield is obtained by using cooled U-tubes for the reaction. The electrodes can be made of copper, nickel, copper–nickel alloy, or steel, since none of these materials has a significant influence on the yield of NF_3. Electrodes made of silver or silver–copper alloy disintegrate rapidly in an atmosphere of fluorine, but they give a higher yield of NF_3 than (say) copper electrodes[40]. Varying the fluorine to nitrogen ratio in the initial mixture of gases does not lead to the synthesis of additional products (other than nitrogen trifluoride). The yield of NF_3 is almost independent of the composition of the initial mixture, and increases with the energy dissipated per unit volume of reacting gases to a maximum of 60–70%.[31] Because of its high energy consumption the plasmo-chemical method of synthesis of NF_3 has only limited preparative value. Fluorination of $^{15}N_2$ in a glow discharge has been used[41] to prepare $^{15}NF_3$. Nitrogen trifluoride has been synthesised from the elements also in a barrier discharge (though in low yield)[42], and in a pulsed u.h.f. discharge[43].

2. Dissociation of Nitrogen Trifluoride

Nitrogen trifluoride is unstable in electrical discharges, and easily dissociates into fluorine and nitrogen[31]. The dissociation is reversible, and if the flow rate of the NF_3 through the reactor is slow a limiting concentration of the dissociation products is observed, which depends (among other things) on the strength of the discharge current. For example, for a pressure of 15 mmHg in the glow discharge the degree of dissociation is 70, 90, and 96% for discharge currents of 12, 25, and 40 mA respectively[44]. The limiting degree of dissociation of NF_3 in a barrier discharge under circulating flow conditions[42] is 98%; almost complete decomposition of the NF_3 is obtained also in a u.h.f. discharge[43].

The effect of added fluorine, nitrogen, and oxygen on the decomposition of NF_3 has been studied[45] in a glow discharge without cooling the walls of the reactor in liquid nitrogen. Fluorine inhibits the decomposition slightly, probably by displacing the reaction $NF_3 \rightleftharpoons F + NF_2 \rightleftharpoons 2F + NF \rightleftharpoons 3/2F_2 + 1/2N_2$ towards the regeneration of nitrogen trifluoride. Addition of nitrogen accelerates the decomposition of nitrogen trifluoride, possibly by transfer to the NF_3 molecules of the energy of the electronically excited N_2 molecules: it is well known[46] that NF_3 can be decomposed by active nitrogen, though less readily than ammonia. Addition of oxygen also accelerates the decomposition of NF_3. Under these conditions the system contains fluorine, nitrogen, NO_2, and (in some experiments) N_2O_5. The reason for the absence of nitryl fluoride is not clear, since mixtures of NO_2 and fluorine are known[47] to give FNO_2 very readily by the reactions

$$NO_2 + F_2 \rightarrow FNO_2 + F, \quad NO_2 + F + M \rightarrow FNO_2 + M.$$

The tendency of nitrogen trifluoride to dissociate in a discharge allows this material to be used as a fluorinating agent. Thus, a mixture of NF_3 and O_2 in a tube cooled in liquid nitrogen gave oxygen fluorides at a current of 20 mA and 0.6 mmHg pressure[48], though the formation of trifluoramine oxide (F_3NO) was not detected. Yet, this compound was later synthesised by exactly the same reaction (NF_3 and O_2 in a discharge tube at 77 K: see, for example, Ref. 49). The action of a glow discharge on a mixture of bromine and NF_3 produces bromine fluorides[50]. Bromodifluoramine $BrNF_2$, a possible product of the reaction between Br atoms and NF_2 radicals, is not formed in a glow discharge. The NF_2 radicals formed by the decomposition of NF_3 may be in an unstable excited state which rapidly breaks down. The reaction between NF_3 and chlorine in a microwave discharge gave ClF and nitrogen, but not $ClNF_2$ or Cl_2NF.[51]

3. Synthesis of Difluorodiazine and Tetrafluorohydrazine

Difluorodiazine N_2F_2, which can exist as *cis*- and *trans*-isomers, is formed in trace quantities during the synthesis of NF_3 from the elements in a barrier discharge. Tetrafluorohydrazine (N_2F_4) also could not be obtained in reasonable yield, either from fluorine and nitrogen or from the decomposition of nitrogen trifluoride. One of the factors opposing the synthesis of N_2F_2 and N_2F_4 in discharges is the instability of these compounds in the presence of fluorine,

with which they react to give nitrogen trifluoride. Difluorodiazine N_2F_2 frozen on the wall of the discharge tube at 77 K rapidly reacts with fluorine in a glow discharge to give NF_3. The reaction between N_2F_4 and OF_2 in a discharge at 77 K gives NF_3, NOF, and NO_2F.[39] N_2F_2 and N_2F_4 can be prepared from nitrogen trifluoride in a discharge tube if a fluorine acceptor (for example, mercury) is added[31,52].

4. Synthesis of Trifluoramine Oxide

The synthesis of trifluoramine oxide F_3NO was reported[53-55] in 1966, though there is evidence in the Patent literature that the compound has been known in some laboratories since 1961 to 1962. F_3NO can be synthesised by plasmo-chemical and photochemical methods as well as by methods not involving radiation or low-temperature plasmas.

Different combinations of the basic components (nitrogen, oxygen, and fluorine) can be used for the synthesis of F_3NO in electrical discharges: $N_2+O_2+F_2$,[56] $N_2+OF_2+F_2$,[57] NF_3+OF_2,[57-60] NF_3+O_2,[49,55,61,62] NF_3+N_2O,[61] and NO_2+F_2.[56] A calculation[36,63] based on published thermodynamic data[35] shows that the N + O + F system at equilibrium may contain substantial amounts of F_3NO, the shape of the equilibrium diagram being very dependent on the N : O : F ratio. The mole fraction of F_3NO in the system at equilibrium is relatively high only at 200–300 K, and falls off very steeply at higher temperatures. Since F_3NO is stable at low temperatures it is essential to quench the products at the conclusion of the plasmo-chemical preparation of this compound. The synthesis of F_3NO in a glow discharge is carried out in tubes cooled to 77 K by immersing the reaction volume either wholly or partly in liquid nitrogen. Attempts to "extract" the F_3NO from the discharge and to condense it in a remote trap were unsuccessful.

The yield of F_3NO from nitrogen trifluoride and oxygen[49,55,62,64] is 10–15%, with ~70% utilisation of the NF_3. In addition to F_3NO the reaction produces oxygen fluorides, oxides of nitrogen, and ozone. Ozone formation can be suppressed by using an excess of NF_3 (for example, by using $NF_3 : O_2$ ratios between 2 : 1 and 6 : 1 in the initial mixture[62]). The synthesis of F_3NO from mixtures of NF_3 and OF_2 does not differ in principle from the synthesis from NF_3 and O_2, since the OF_2 merely acts as a source of oxygen by decomposing into its elements in the discharge. Trifluoramine oxide has been prepared in 20–40% yield from an $NF_3 : OF_2 : Ar = 1 : 1 : 2$ mixture[65].

Mixtures of fluorine, nitrogen, and oxygen are not a very convenient reagent for the preparation of F_3NO in spite of the ready availability of the starting materials. When these mixtures are used the formation of F_3NO is suppressed by a competing reaction: the formation of O_2F_2, which consumes 94 to 97% of the oxygen reaching the discharge (assuming an $F_2 : N_2 : O_2$ ratio of 3 : 1 : 1 in the initial gas mixture)[64,66]. The yield of F_3NO cannot be improved by adding an excess of oxygen: this could merely convert the whole of the fluorine present in the system into O_2F_2.

The reaction between fluorine and nitrous oxide has been studied in detail[66]. The extent of conversion of N_2O into F_3NO, calculated by the equation $N_2O + 3/2F_2 = F_3NO + 1/2N_2$, is almost independent of the composition of the mixture, and goes through a maximum (~20–22%) as the flow rate of the gas is increased. Up to 40–50% of the oxygen formed by the dissociation of N_2O reacts with the fluorine to give O_2F_2: ozone formation is negligible, making this method of synthesis safer than the preparation of F_3NO from NF_3 and O_2. In the absence of an electrical discharge the reaction between fluorine and nitrous oxide at 573–1073 K produces a mixture of FNO and NF_3.[67]

Trifluoramine oxide has been obtained in small amounts (0.5 mmole h^{-1}) from a mixture of N_2, O_2, and F_2 (1 : 1 : 3) in a microwave discharge at a pressure of ~0.5 mmHg.[68] The low yield of F_3NO is probably due to the low power of the microwave source used, which prevented the use of higher pressures. Another possible reason for the low yield is the difficulty of synthesising F_3NO from the elements, which was mentioned above.

Thus the plasmo-chemical synthesis of F_3NO is fairly laborious, offers only a moderate yield, and is accompanied by the formation of large amounts of side products. The photochemical method of preparing F_3NO[69-71] is similar in many ways to the plasmo-chemical methods and has an even lower yield. The most promising method appears to be the combustion of nitric oxide in fluorine in a flow reactor[72]. All methods of synthesis of F_3NO apparently include the following main steps: 1) formation of nitric oxide, 2) fluorination of nitric oxide in nitrosyl fluoride [$NO + F(F_2) \rightarrow NOF(+F)$], 3) fluorination of the nitrosyl fluoride ($NOF + 2F \rightarrow F_3NO$). The nitric oxide may be introduced as a reactant or formed in the plasma (by the oxidation of nitrogen or by the decomposition of nitrous oxide).

5. Synthesis of Tetrafluoro-ammonium Salts

Even quite recently the synthesis of stable tetrafluoroammonium salts was believed to be impossible. According to Wilson[73], only $NF_4^+BF_4^-$ could have enough thermal stability to exist as a stable compound at temperatures below 153 K. However, two papers[74,75] published in 1966 reported the preparation of the salts $NF_4^+AsF_6^-$ and $NF_4^+SbF_6^-$, which are stable at room temperature but rapidly decompose at temperatures above 543–573 K. In 1970 the compound $NF_4^+BF_4^-$ was synthesised[76], and found to be stable up to 513–623 K. In recent years a few more salts containing the NF_4^+ cations have been prepared. The tetrafluoro-ammonium compounds are powerful oxidising agents: they can be used, in principle, as components of solid rocket fuels[77], in gas generating apparatus[78,79], and in laser technology[80,81]. Tetrafluoroammonium hexafluoro-arsenate and tetrafluoroborate have been synthesised in a glow discharge.

The compound NF_4AsF_6 was prepared by circulating a mixture of NF_3, AsF_5, and F_2 (1 : 1 : 2) in a glow discharge apparatus with a discharge tube cooled to 195 K.[31,75,82,83] In very long (~40 h) experiments with inadequate cooling the reactor wall suffered serious corrosion, forming salts with oxygenated cations which contaminated the desired product. In an experiment[84] with a high-pressure mercury lamp irradiating an equimolar mixture of NF_3, AsF_5, and F_2 in a quartz vessel at room temperature the compound $O_2^+AsF_6^-$ was obtained instead of NF_4AsF_6 as a result of corrosion of the walls of the vessel. At 77 K the same reactants in a quartz reactor irradiated with light from a 900 W mercury lamp yielded NF_4AsF_6 at a rate greater than 1 g h^{-1}.[81]

Attempts to synthesise NF_4BF_4 in a glow discharge with a reactor cooled to 195 K proved unsuccessful[85,86]: instead of NF_4BF_4, $O_2^+BF_4^-$ was obtained together with a salt which hydrolysed to give nitrogen oxides. In order to obtain NF_4BF_4 from NF_3, BF_3, and fluorine the reactor walls must be cooled in liquid nitrogen[76,87-89]. The synthesis is carried out as follows: the NF_3 and BF_3 are condensed on the wall of a U-shaped discharge tube, and gaseous fluorine is slowly allowed to flow through the discharge at 30–55 mmHg with a current of 30 mA. After 1 h of discharge a fluorine flow of 400 cm^3 h^{-1} produces ~3 g of NF_4BF_4 in a yield approaching 100%. Up to 3 g h^{-1} of NF_4BF_4 can be obtained by an improved variant of the photochemical method

of synthesis from NF_3, BF_3, and F_2 at 77 K in a reactor made of steel and sapphire[81].

Reactions in which NF_3^+ or F^+ ions give NF_4^+ (for example, $NF_3^+ + F \rightarrow NF_4^+$, or $NF_3 + F^+ \rightarrow NF_4^+$) are possible, in principle, in an electrical discharge, but not in the photochemical or thermal synthesis of tetrafluoro-ammonium salts, since the u.v. energy or the thermal energy of the reactants at 373 to 473 K is insufficient to ionise NF_3 or F. In this context it is interesting to consider the suggestion[84] that the active particles responsible for the oxidation of NF_3 could be the radicals $AsF_6^\cdot$, which have a high electron affinity and are formed from a fluorine atom and a molecule of the Lewis acid AsF_5. The reaction between $AsF_6^\cdot$ and NF_3 would give first $NF_3^+AsF_6^-$ and then $NF_4^+AsF_6^-$ (by the addition of a fluorine atom).

The possible existence of the radicals $AsF_6^\cdot$, $SbF_6^\cdot$, $Sb_2F_{11}^\cdot$, and the cation radical $NF_3^{+\cdot}$ was confirmed experimentally[90] by γ-radiolysis of the salts NF_4AsF_6 and $NF_4SbF_6.0.8SbF_5$ at 77 K. It was also shown that $NF_3^{+\cdot}$ can be formed as an intermediate during the photochemical synthesis of NF_4AsF_6 and NF_4BF_4 from mixtures of NF_3, F_2, and a Lewis acid[91]. The radical $BF_4^\cdot$ was not detected during the radiolysis of NF_4BF_4, possibly because of its low thermal stability. The instability of $BF_4^\cdot$ may also explain the failure to obtain NF_4BF_4 in a glow discharge at 195 K.[85,86]. A study[92] of the thermal decomposition of the salts NF_4BF_4 and NF_4AsF_6 finally led to the rejection of the mechanism of formation of NF_4^+ through the formation of radicals of the $AsF_6^\cdot$ type and their reaction with NF_3 molecules, and to its replacement by the mechanism

$$F_2 \rightleftarrows 2F, \quad F + NF_3 \rightleftarrows NF_4,$$
$$NF_4 + AsF_5 \rightleftarrows NF_3^+AsF_6^-, \quad NF_3^+AsF_6^- + F \rightleftarrows NF_4^+AsF_6^- .$$

III. SYNTHESIS OF OXYGEN FLUORIDES

The reaction between fluorine and oxygen and the synthesis of oxygen fluorides in a glow discharge are discussed in earlier reviews[31,32]. The plasmo-chemical method was, for a long time, the only method of preparing the compound dioxydifluoride O_2F_2. In 1969 a radiation-chemical synthesis of O_2F_2 was reported[32], and more recently it was suggested that the compound can be obtained by irradiating a mixture of $O_2 + F_2$ or $OF_2 + F_2$ at 77 K with light from a mercury lamp (365 nm)[93] or by fluorinating the oxygen with thermocatalytically generated atomic fluorine[94].

The reality of the existence of higher members of the polyoxydifluoride series O_nF_2 ($n = 2$–6) had been questioned (see previous reviews[31,32]). Pshezhetskii and coworkers[95] doubt the existence of tetraoxydifluoride O_4F_2 as a pure compound. The electronic absorption spectrum of the product obtained by a method[96] claimed to give O_4F_2 in a glow discharge was assigned to a mixture of O_2F_2 and the radicals $O_2F^\cdot$. The compound of empirical formula O_4F_2 is thought[95] to be the radical $O_2F^\cdot$, at least in dilute solutions (in liquid argon, oxygen, or CF_4). The reaction between fluorine and oxygen in a glow discharge with reactor walls cooled to 77 K or below apparently gives only one of the "polyoxydifluorides": the dioxydifluoride, which may contain the $O_2F^\cdot$ radical in concentrations anomalously high for a free radical.

The action of a barrier discharge on a fluorine–oxygen mixture has been studied[97,98]. Pyrex glass ozonisers made of three coaxial tubes were used as reactors. Power was supplied to the ozonisers from an audio-frequency signal generator and amplifier; the reaction was studied in a circulating regime with the fluorine–oxygen mixture at an initial pressure of 100–600 mmHg. The ozoniser wall was cooled in running water, and the gas flow from the ozoniser was led by a connecting tube to a trap cooled in liquid nitrogen ~50 cm away from the ozoniser. A yellow or orange solid was condensed in the cold trap, though in some experiments the condensate (at 77 K) contained a dark red liquid. The composition of the low-temperature condensate obtained from an ozoniser in which the discharge gap was 1 mm wide varied according to the composition of the initial gas mixture, the power of the discharge, the time for which the gas was circulated, and the initial pressure of the gas. The O : F atomic ratio in the condensate varied between 1.1 and 2.04. The most probable combination of oxygen fluorides (to account for a chemical analysis of $O:F = 1.1$–2.04) is the mixture $O_2F_2 + (O_2F)_x$ (mistaken for "O_4F_2" when $x = 2$). The oxygen content in the condensate tends to increase with the circulation time of the initial gas mixture and with its oxygen content, and with a decrease in the power of the discharge and in the initial pressure in the reactor. On heating the tube connecting the ozoniser to the cold trap from room temperature to 323–333 K the rate of formation of condensate in the trap falls off very steeply, though some condensation persists even under conditions clearly unsuitable for the transport of "cryogenic" compounds. The O : F ratio in the condensate remains close to 2 under these conditions, i.e. the condensate approaches the composition "O_4F_2" corresponding in reality to any agglomerate of the $(O_2F)_x$ type.

Since O_2F_2 is thermally more stable[31] than "O_4F_2" the enrichment of the condensate in the "tetra-oxydifluoride" on heating the connecting tube is unexpected. Evidently, the $O_2F^\cdot$ radicals are more stable than the O_2F_2 molecules, and these molecules are decomposed preferentially in the heated gas stream, leading to a change in the $O_2F_2 : O_2F^\cdot$ ratio in favour of the $O_2F^\cdot$ radicals and to a corresponding change in the composition of the condensate. The $O_2F^\cdot$ radicals are stable towards F_2 molecules, and they are fluorinated to O_2F_2 only under the influence of atomic fluorine. The compound dioxygenyl hexafluoroarsenate $O_2^+AsF_6^-$, which dissociates on heating with evolution of $O_2F^\cdot$,[99] has been used recently to prepare $O_2F^\cdot$ radicals and to study their properties.

The condensate obtained from an ozoniser with a discharge gap 0.5 mm wide contains, in addition to the unstable oxygen fluorides, the stable compound oxygen difluoride[98]. The synthesis of $OF_2^\cdot$ is very slow: under the most favourable experimental conditions the yield of $OF_2^\cdot$ was only 2 mmole h^{-1}. The low rate of formation of $OF_2^\cdot$ is explained by the presence of a competing reaction (the synthesis of the unstable oxygen fluorides) and by the difficulty of stabilising the oxygen difluoride in the discharge apparatus of the chosen type.

As a method of synthesis of oxygen fluorides the barrier discharge is inferior to the glow discharge not only in terms of apparatus complexity and of yield, but also because the composition of the condensate is more sensitive to experimental conditions.

IV. SYNTHESIS OF THE HALOGEN FLUORIDES AND OF CHLORINE OXYTRIFLUORIDE

The compounds of fluorine with chlorine, bromine, or iodine are prepared from the elements at room temperature or with moderate heating[100]; many methods of preparing chlorine oxide fluorides are also known. Electric discharges

have been used in the search for methods of synthesis of higher halogen fluorides and of new chlorine oxyfluorides.

1. Synthesis of Chlorine Pentafluoride

An unsuccessful attempt to prepare ClF_5 from ClF_3 and fluorine in an electrical discharge was reported[39] in 1957. The first disclosure[101] of the synthesis of chlorine pentafluoride at elevated temperature and pressure was in 1963; a patent application for the preparation of ClF_5 in a discharge[102] appeared in the same year. In the glow-discharge synthesis[102,103] a mixture of fluorine and chlorine is passed through a U-shaped discharge tube with copper electrodes (cooled to 195 K), and the gases from the outlet are taken to a trap at 77 K. The pressure (30 mmHg) and current (30 mA) in the discharge are kept constant. The reaction products (ClF, ClF_3, and ClF_5) can be separated by low-temperature sublimation. Fluorine can be made to react with chlorine both in a glow discharge (with direct current or at mains frequency) or in an h.f. discharge[102]. Instead of fluorine and chlorine, binary compounds of fluorine and chlorine can be used[102] for the synthesis of ClF_5 (ClF, ClF_3, NF_3, N_2F_2, N_2F_4, NCl_3) as long as the number of fluorine atoms in the initial mixture is in 1–10 fold stoichiometric excess over the number needed to form ClF_5.

The salt $ClF_6^+PtF_6^-$, whose cation can be formally considered to have been derived from the hypothetical chlorine fluoride ClF_7, has been described (see, for example, Ref.104). It was synthesised by photochemical oxidation of ClF_5, using PtF_6, but attempts to produce ClF_6^+ in a glow discharge were unsuccessful[104]. A glow discharge in a reactor made of Pyrex glass, at 195 K and 20–50 mmHg pressure, yields $ClF_2^+BF_4^-$ (but not $ClF_6^+BF_4^-$) from a mixture of $BF_3 + F_2 + ClF_5$ (1:1 and 42:1). Obviously, the ClF_5 dissociates with formation of ClF_3, which reacts with the BF_3 present in the system to give crystalline $ClF_2^+BF_4^-$.[104,105]

2. Synthesis of Bromine Pentafluoride

The reaction between bromine and fluorine in a glow discharge is carried out by freezing bromine in a U-shaped discharge tube at 195 K and adding fluorine to the discharge, either continuously or in portions, while maintaining a pressure of 20–25 mmHg and a discharge current of 20–30 mA.[50] As the reaction proceeds the deeply coloured bromine is converted into the colourless bromine pentafluoride. An 80 to 85% extent of conversion of the Br_2 (calculated as BrF_5) is reached in a few minutes, but the reaction then slows down, and quite long times are needed for the reaction to go to completion. The final yield of BrF_5 is almost 100%. Cooling the walls of the discharge tube with liquid nitrogen lowers the rate of fluorination very strongly, probably by suppressing the renewal of the frozen bromine surface and thus making the underlying layers of condensate inaccessible to the fluorine. The reaction between fluorine atoms and bromine molecules also gives bromine pentafluoride[9].

Unsuccessful attempts have been made to prepare bromine heptafluoride[106]: apparently, BrF_7 (like ClF_7) is unstable towards dissociation into the pentafluoride and fluorine, even at very low temperatures. However, the salts $BrF_6^+AsF_6^-$ and $BrF_6^+Sb_2F_{11}^-$, which contain the BrF_6^+ cation, are known[106]. They are prepared by oxidising bromine pentafluoride with $Kr_2F_3^+$ or KrF^+. The resulting BrF_6^+ is one of the strongest oxidising agents known, and it can easily oxidise O_2 to O_2^+ or xenon to XeF^+ under normal conditions.

3. Synthesis of Chlorine Oxytrifluoride

Chlorine oxytrifluoride F_3ClO was first synthesised in 1965 by a group of workers in the USA,[107] and the synthesis was later confirmed by an independent group in France[108] in 1970. Several methods of preparing F_3ClO have since been reported (see, for example, Ref.109), but they all have serious drawbacks: they are laborious, the reactants are not easily available, the yield of product is low, etc.

Chlorine oxytrifluoride, like trifluoramine oxide, can be prepared in an electrical discharge. In addition to their formal similarity, the reactions leading to the synthesis of F_3ClO and F_3NO have one important feature in common: the need to stabilise the end product very effectively. The quenching and storage of F_3ClO is complicated by the very high reactivity of this compound, which attacks glass or quartz even at temperatures below 273 K. The synthesis of F_3ClO in an electrical discharge has not been studied fully. The compound was first prepared[107] by freezing Cl_2O at 77 K on a Pyrex glass U-tube reactor and passing fluorine at 20 mmHg pressure through the discharge. The products contained ClF_5 (~45 mole %), $FClO_2$, ClF_3, and only 1–2% of F_3ClO. The formation of F_3ClO from ClF_5 and O_2 in a glow discharge with reactor walls cooled to 77 K has been reported[105]. If the wall temperature is raised to 195 K, a strong acceptor of fluoride ions (like BF_3) is needed to fix the F_3ClO in the form of the salt $F_2ClO^+BF_4^-$. Low-temperature fluorination of the salt $ClO_2^+BF_4^-$ in a glow discharge also gives $F_2ClO^+BF_4^-$.[110] Chlorine oxytrifluoride is one of the products of the reaction of perchloryl fluoride $FClO_3$ with fluorine in a glow discharge at 77 K.[105] The action of a glow discharge on a mixture of F_2, Cl_2, and O_2 yields chlorine oxytrifluoride, but in a yield not exceeding 6%.[105] Similarly low yields were reported (see above) for the preparation of trifluoramine oxide from its elements.

V. SYNTHESIS OF THE INERT GAS FLUORIDES

Early work on the synthesis of krypton and xenon fluorides is reviewed in Ref.31. The most difficult to prepare is krypton difluoride, due to the low reactivity of krypton and the low thermal stability of KrF_2. Yields of ~1 g h^{-1} were obtained[111] in the synthesis of KrF_2 in a glow discharge at a current of 10 mA. When the reactor is at 123 K krypton difluoride is not formed. The use of a barrier discharge in a reactor cooled in liquid oxygen or nitrogen gave a yield[112] of KrF_2 of 50 mg kW^{-1} h^{-1}. In a photochemical method[113] of preparing KrF_2 by irradiating a mixture of krypton and fluorine (condensed at 77 K) with light from a mercury lamp the yield of KrF_2 was 4.7 g after 48 h. The photochemistry of krypton difluoride was studied also by Legasov and coworkers[114–116]. KrF_2 is produced at rates of up to 6 kg h^{-1} by treating krypton frozen at 77 K with atomic fluorine generated by a heated nickel catalyst[117]. The reaction between krypton and fluorine in a glow discharge in the presence of antimony pentafluoride[118] gave $KrF^+SbF_6^-$ if the reactor walls were cooled with liquid nitrogen and the discharge current was 10–30 mA.

Xenon difluoride has been prepared in almost 100% yield from a mixture of fluorine and xenon in a glow discharge at 196 K.[119] In the presence of an excess of fluorine XeF_4 is formed, but the tetrafluoride cannot be prepared free from traces of XeF_2 in a glow discharge. A mixture of fluorine and xenon (3:1) was shown[120] to yield XeF_2 contaminated with $XeF_2.XeF_4$ in the early stages of the reaction, and XeF_6 containing a small amount of $XeF_2.XeF_4$ in the later stages. The absence of XeF_4 crystals at all stages of the reaction

was demonstrated by X-ray phase analysis. The authors conclude[120] that the xenon fluorides are formed by the successive fluorination of XeF_2 to XeF_4, and XeF_4 to XeF_6, at rates one order of magnitude lower for each step.

XeF_4 has been synthesised (in yields of up to 39.3 g h^{-1}) by treating solid xenon in a "fluidised" bed with atomic fluorine generated in an h.f. discharge (8 MHz, 0.1–2 kW).[29] Xenon difluoride has been prepared in a pulsed high-pressure discharge with a current of amplitude 50 kA and frequency 70 kHz.[121] The photochemical reaction of xenon with an excess of fluorine ($Xe:F_2 = 1:4–6$) yields XeF_4 at room temperature[122]; the reaction takes place in two steps, and the fluorination of XeF_2 to XeF_4 is ~20 times slower than the fluorination of Xe to XeF_2. The interaction of F atoms with XeF_2 or XeF_4 was not detected in a kinetic study[9] of the reactions of atomic fluorine: the reason is not clear.

Xenon dichloride for spectroscopic work has been prepared by condensing on a cold surface (10–15 K) a mixture of xenon and chlorine which had passed through a microwave discharge[123].

VI. OTHER REACTIONS OF FLUORINE AND FLUORIDES

Many element–organic compounds containing trifluoromethyl groups can be synthesised by using an h.f. discharge: HgR_2, RHgX, R_2Te_2, R_2Te, SnR_4, GeR_4, BiR_3 (where $R = CF_3$, X = Cl, Br, I).[124–126] The $CF_3^{\cdot}$ radicals are obtained by the dissociation of hexafluoroethane in an h.f. discharge (8.6 to 13.6 MHz) at 0.5–2 mmHg pressure. The course of the reaction is strongly influenced by the power dissipated in the discharge. The dissociation of C_2F_6 into $CF_3^{\cdot}$ radicals requires only 20–25 W, and the use of higher powers causes more substantial decomposition of the C_2F_6 molecule with formation of fluorine atoms and $CF_2^{\cdot}$ radicals. The C–C bond is much less stable than the C–F bond in the C_2F_6 molecule, and the power of the discharge is used initially in breaking the C–C bonds, thus allowing C_2F_6 to be used as a source of pure $CF_3^{\cdot}$ radicals. These radicals can react with the halides of mercury, tellurium, tin, etc. to give the corresponding element–organic compounds. The reactions are slow: typical rates for the synthesis of HgR_2, SnR_4, and BiR_3 are 8, 1, and 0.2 g day^{-1} respectively. The unstable compound $Xe(CF_3)_2$ has been obtained[127] by the reaction of XeF_2 with $CF_3^{\cdot}$ radicals generated from C_2F_6 in the plasma of an h.f. discharge.

Hexafluoro-acetone is an alternative source of CF_3 radicals in an h.f. discharge. The concentration of $CF_3^{\cdot}$ radicals increases linearly with the function $W(P/P_0)^{1/2}$, where W is the power of the discharge (3–24 W), P is the partial pressure of $(CF_3)_2CO$ (0.016–0.064 mmHg), and P_0 is the pressure of the mixture of $(CF_3)_2CO$ and the argon diluent (0.4 to 0.9 mmHg).[128] On the assumption that the $CF_3^{\cdot}$ radicals disappear only by homogeneous recombination the rate constant of the radical formation reaction $(CF_3)_2CO \rightarrow 2CF_3^{\cdot} + CO$ is proportional to the square of the power. Hexafluoro-acetone in an h.f. discharge also acts as a source of the relatively long-lived difluoromethylene radicals (also obtained from CF_4 in a glow discharge and from perfluorocyclobutane in an h.f. discharge)[129]. The $CF_2^{\cdot}$ radicals play an important role in the decomposition of polytetrafluoroethylene in a microwave discharge[130]. In a glow discharge with the reactor cooled to 77 K the compound tris(trifluoromethyl)-hydroxylamine $(CF_3)_2NOCF_3$ yields both $CF_3^{\cdot}$ radicals and fluorine atoms, forming CF_4, COF_2, CF_3NCF_2, C_2F_6, $(CF_3)_2NF$, and $(CF_3)_3N$.[131] The application of a barrier discharge to CF_3PH_2 produces perfluorohydrocarbons, and also the trifluoromethylphosphines $(CF_3)_2PH$, $(CF_3)_3P$, and $CF_3PHPHCF_3$; from $(CF_3)_2PH$ the compounds CF_3PH_2, $(CF_3)_3P$, and $(CF_3)_4P_2$ have been obtained[132].

Polymeric carbon monofluoride $(CF_x)_n$ can be prepared by the reaction between powdered graphite and a fluorine plasma[133,134]. The reaction is carried out in a pseudo-condensed layer at a pressure of 2–5 mmHg. A stream of fluorine passes through the h.f. discharge (20 MHz, 480 W) and reacts slowly with the powdered graphite, giving a snow-white polymeric powder of composition $CF_{1.19}$. A substance of composition $CF_{0.68}$ is also formed, as well as the volatile side-product CF_4. The $(CF_x)_n$ product is almost black for $x = 0.68–0.8$, grey for $x = 0.8–0.95$, and white for $x = 0.95–1.12$. White samples are stable in air at up to ~873 K. Polymeric carbon monofluoride can be used as a high-temperature lubricant in oxidising atmospheres and for frictional components carrying a high load; another potential application of this compound is as a cathode material for high-capacity accumulators.

The silicon analogue of the carbene (SiF_2) is formed in small amounts during the dissociation of silicon tetrafluoride in a glow discharge[135]. Linear and cyclic fluorosiloxanes have been detected mass-spectrometrically[136] among the products of a microwave discharge in SiF_4. A fluorosiloxane polymer of composition $(SiO_{1.5}F)_n$ was obtained from the reaction of SiF_4 with oxygen in a microwave discharge[20]. Trifluorosilane decomposes in a glow discharge, giving SiF_4, Si_2F_6, and a polymeric compound[137].

Sulphur tetrafluoride gives SF_6 in 80% yield in the plasma of a microwave discharge[138]. Sulphur hexafluoride is formed also by the decomposition of S_2F_{10}, SF_5Cl, or $(SF_5)_2O_2$ in a microwave discharge, and the reactions of SF_6, SF_2F_{10}, or SF_4 with chlorine give SF_5Cl.[139] Passing a mixture of selenium hexafluoride and chlorine through a u.h.f. discharge gives only SeF_4.[139] The plasmo-chemical decomposition of SF_6 in a quartz reactor can yield sulphur oxide fluorides formed by the attack on the reactor walls. Thus, substantial amounts of SOF_4, SO_2F_2, SOF_2, and also SiF_4 have been obtained[140] during the decomposition of SF_6 in a quartz reactor by h.f. discharge. A mass spectrometric study of the interaction of SF_6 with the nitrogen plasma of an h.f. discharge revealed the presence of SF_2 as one of the main components of this plasma system, whereas nitrogen fluorides were formed only in trace amounts[141]; the reaction of SF_6 with an oxygen plasma gave OF_2, SO_2, and SOF_2.

Sulphur hexafluoride or a mixture of SF_6 with oxygen, and also carbon tetrafluoride and other fluorocarbons, have been used as the plasma-forming gases in the plasmo-chemical etching of Si, SiO_2, and photoresist in integrated circuit technology (see, for example, Ref. 142). Both fluorine atoms and fluorine molecules, produced by the decomposition of the fluorides in the discharge, contribute to the etching process[143].

Boron trifluoride (unlike the trichloride) is quite stable in electrical discharges. Nevertheless it can undergo changes under the influence of a discharge: thus, the yield of BF_2NH_2 by the reaction between BF_3 and ammonia can be increased markedly by activating the boron trifluoride in a microwave discharge of 80 W power[144].

Lower uranium fluorides are formed by the dissociation of uranium hexafluoride in a low-temperature plasma[145]. The stability of the discharge in UF_6 is determined by the gas pressure and by the frequency of the generator: at 10 MHz the discharge is stable up to 15–20 mmHg, at 17 MHz up to 30 mmHg, and at 2450 MHz frequency a stable discharge can be obtained at atmospheric pressure. The reaction of atomic fluorine generated in an h.f. discharge with uranium tetrafluoride has yielded up to 240 g h^{-1} of UF_6.[29] The fluorination of platinum with atomic fluorine gives PtF_6.[29]

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The reactions of fluorine and of the fluorides discussed above have been carried out in the non-equilibrium plasma of a glow discharge and of h.f., microwave and barrier discharges. The primary effect of an electrical discharge appears to be the generation of atomic fluorine by the dissociation of fluorine (or fluoride) molecules. The fluorine atoms then react with the other component, which may be located (in a gaseous or a condensed state) in the region where the fluorine atoms are generated or outside this region. Furthermore, the discharge may also activate the second component of the reaction (though this is not always a requirement in fluorination reactions). For example, the synthesis of O_2F_2 in an electrical discharge does not require special activation of the oxygen molecules, and the same is true of the fluorination of oxygen to O_2F_2 (in a reactor cooled in liquid nitrogen) by atomic fluorine generated on a nickel catalyst. Similarly, the synthesis of KrF_2 and XeF_2 in a glow discharge does not require activation of the krypton or xenon atoms.

The yield of the reaction products depends on several factors, such as the thermal stability of the product, its stability towards the discharge, and its inertness towards the apparatus walls. The thermally unstable compound O_2F_2, which has a vapour pressure of 0.01 mmHg at 105 K, condenses on the reactor wall when synthesised in a glow discharge and can be prepared in quantitative yield, whereas oxygen difluoride, though stable at up to ~480 K, has a vapour pressure of ~1 mmHg at 77 K and cannot be prepared in a glow discharge: it is not found among the products, possibly as a result of its decomposition in the gas phase under the influence of the discharge.

Fluorination in a discharge tends to give the higher fluorides, though the O + F system is exceptional in this respect and yields its highest and most stable fluoride (OF_2) only in a barrier discharge and in small yield. In the N + O + F and Cl + O + F systems only two members of the large group of oxide fluorides of nitrogen and chlorine have been obtained by plasmo-chemical methods: F_3NO and F_3ClO. This may be due to low stability of the other oxide fluorides in a glow discharge.

The equilibrium low-temperature plasma is not very attractive as a reaction medium for fluorine and the fluorides, though it could be used for pyrolysis reactions involving (for example) chlorofluorocarbon compounds.

REFERENCES

1. H.E.Radford, V.W.Huges, and V.Beltran-Lopez, Phys.Rev., 1961, **123**, 153.
2. R.J.McIntyre and F.K.McTaggart, Austral.J. Chem., 1971, **24**, 2683.
3. D.E.Rosner and H.D.Allendorf, J.Phys.Chem., 1971, **75**, 308.
4. C.E.Kolb and M.Kaufman, J.Phys.Chem., 1972, **76**, 947.
5. G.Schatz and M.Kaufman, J.Phys.Chem., 1972, **76**, 3586.
6. D.E.Rosner and J.P.Starkey, J.Phys.Chem., 1973, **77**, 690.
7. J.W.Bozzelli, C.E.Kolb, and M.Kaufman, J.Chem. Phys., 1973, **59**, 3669.
8. P.S.Ganguli and M.Kaufman, Chem.Phys.Letters, 1974, **25**, 221.
9. E.H.Appelman and M.A.A.Clyne, J.Chem.Soc. Faraday Trans.I, 1975, 2072.
10. M.A.A.Clyne, D.J.McKenney, and R.F.Walker, Canad.J.Chem., 1973, **51**, 3596.
11. R.E.Huffman, J.C.Larrabee, and Y.Tanaka, J. Chem.Phys., 1967, **47**, 856.
12. A.Persky, J.Chem.Phys., 1973, **59**, 5578.
13. A.Carrington, D.H.Levy, and T.A.Miller, J.Chem. Phys., 1966, **45**, 4093.
14. N.Jonathan, C.M.Melliar-Smith, S.Okuda, D.H.Slater, and D.Timlin, Mol.Phys., 1971, **22**, 561.
15. I.B.Goldberg, H.R.Crowe, and D.Pilipovich, Chem.Phys.Letters, 1975, **33**, 347.
16. W.E.Jones and E.G.Skolnik, Chem.Rev., 1976, **76**, 563.
17. A.C.Lloyd, Internat.J.Chem.Kinetics, 1971, **3**, 39.
18. V.S.Artyunov, L.S.Popov, and A.M.Chaikin, Kinetika i Kataliz, 1976, **17**, 286.
19. V.S.Artyunov and A.M.Chaikin, Kinetika i Kataliz, 1977, **18**, 316.
20. D.R.Secrist and J.M.MacKenzie, J.Polymer Sci., 1966, **B4**, 537.
21. V.S.Artyunov and A.M.Chaikin, Kinetika i Kataliz, 1977, **18**, 321.
22. J.Wilson, H.L.Chen, W.Fyfe, R.L.Taylor, R.Little, and R.Lowell, J.Appl.Phys., 1973, **44**, 5447.
23. J.J.De Corpo, R.P.Steiger, J.L.Franklin, and J.L.Margrave, J.Chem.Phys., 1970, **53**, 936.
24. E.M.Belenov, V.A.Isakov, A.N.Oraevskii, and V.I.Romanenko, Kvantovaya Elektronika, 1974, **1**, 1375.
25. T.L.Porter, J.Chem.Phys., 1968, **48**, 2071.
26. V.V.Zaitsev, E.Yu.Zverevskaya, V.D.Klimov, and P.D.Netyagov, Zhur.Fiz.Khim., 1977, **51**, 1213 [Russ.J.Phys.Chem., 1977(5)].
27. V.V.Zaitsev, E.Yu.Zverevskaya, V.D.Klimov, N.V.Bozhko, and P.D.Netyagov, Khim.Vys. Energii, 1978, **12**, 516.
28. V.V.Zaitsev, E.Yu.Zverevskaya, and V.D.Klimov, Zhur.Fiz.Khim., 1980, **54**, 667 [Russ.J.Phys. Chem., 1980(3)].
29. O.G.Lebedev, M.V.Murashov, and V.N.Prusakov, Khim.Vys.Energii, 1978, **12**, 533.
30. I.D.Chalmers, H.Duffy, and D.J.Tedford, Proc. Roy.Soc., 1972, **A329**, 171.
31. I.V.Nikitin and V.Ya.Rosolovskii, Uspekhi Khim., 1970, **39**, 1161 [Russ.Chem.Rev., 1970(7)].
32. I.V.Nikitin and V.Ya.Rosolovskii, Uspekhi Khim., 1971, **40**, 1913 [Russ.Chem.Rev., 1971(11)].
33. A.V.Pankratov, "Khimiya Ftoridov Azota" (Chemistry of the Nitrogen Fluorides), Izd.Khimiya, Moscow, 1973.
34. A.V.Pankratov, Zhur.Fiz.Khim., 1969, **43**, 403 [Russ.J.Phys.Chem., 1969(2)].
35. "JANAF Thermochemical Tables", National Bureau of Standards, 1971.
36. N.V.Alekseev and I.V.Nikitin, "Tezisy Dokladov Vtorogo Vsesoyuznogo Simpoziuma po Plazmokhimii" (Proceedings of the Second All-Union Symposium on Plasma Chemistry), Riga, 1975, Vol.2, p.166.
37. R.F.Baddour and R.Timmins (Editors), "Application of Plasmas to Chemical Processing" (Translated into Russian), Izd.Mir, Moscow, 1970, p.201.
38. W.Maya, Inorg.Chem., 1964. **3**, 1063.
39. E.W.Lawless and I.C.Smith, "Inorganic High-energy Oxidisers", Dekker, New York, 1968.

40. I.V.Nikitin and V.Ya.Rosolovskii, USSR P. 461 056/1975; Byull.Izobr., 1975, No.7. p.47.
41. I.J.Solomon, J.N.Keith, and A.Snelson, J.Fluor. Chem., 1972/1973, **2**, 129.
42. A.V.Dudin, I.V.Nikitin, and V.Ya.Rosolovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1970, 710.
43. I.V.Nikitin, V.Ya.Rosolovskii, G.V.Lysov, and E.A.Petrov, "Tezisy Dokladov Pyatogo Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Proceedings of the Fifth All-Union Symposium on the Chemistry of Inorganic Fluorides), Dnepropetrovsk, 1978, p.198.
44. I.V.Nikitin, Thesis, Moscow, 1970.
45. I.V.Nikitin and V.Ya.Rosolovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1971, 1603.
46. A.N.Wright and C.A.Winkler, "Active Nitrogen", Academic Press, New York, 1968, p.404.
47. R.L.Perrine and H.S.Johnston, J.Chem.Phys., 1953, **21**, 2202.
48. M.Schmeisser and K.Brändle, Adv.Inorg.Chem. Radiochem., 1963, **5**, 41.
49. W.B.Fox, J.S.MacKenzie, E.R.McCarthy, J.R.Holmes, R.F.Stahl, and R.Juurik, Inorg.Chem., 1968, **7**, 2064.
50. I.V.Nikitin and V.Ya.Rosolovskii, Zhur.Neorg. Khim., 1975, **20**, 263 [Russ.J.Inorg.Chem., 1975(1)].
51. S.S.Christy and G.Mamantov, Internat.J.Mass Spectrosc.Ion Phys., 1970, **5**, 319.
52. J.W.Fraser, J.Inorg.Nuclear Chem., 1959, **11**, 166.
53. N.Bartlett and S.P.Beaton, Chem.Comm., 1966, 167.
54. N.Bartlett., J.Passmore, and E.J.Wells, Chem. Comm., 1966, 213.
55. W.B.Fox, J.S.McKenzie, N.Vanderkooi, B.Sukornick, C.A.Wamser, J.R.Holmes, R.E.Eibeck, and B.B.Stewart, J.Amer.Chem.Soc., 1966, **88**, 2604.
56. W.Maya, US P. 3 320 147/1967; Chem.Abs., 1967, **67**, 55 830.
57. Allied Chemical Corporation, B P. 1 038 840/1966; Chem.Abs., 1966, **65**, 13 272.
58. W.B.Fox and J.S.McKenzie, US P. 3 323 866/1967; Chem.Abs., 1967, **67**, 55 778.
59. W.B.Fox, J.S.McKenzie, and N.Vanderkooi, US P. 3 438 540/1969.
60. W.B.Fox, E.R.Eibeck, and J.S.McKenzie, US P.3 394 998/1968.
61. J.H.Gross, US P. 3 355 469/1971; Chem.Abs., 1971, **74**, 101 281.
62. W.B.Fox and J.S.McKenzie, US P. 3 392 099/1968.
63. N.V.Alekseev and I.V.Nikitin, Khim.Vys.Energii, 1976, **10**, 176.
64. I.V.Nikitin and V.Ya.Rosolovskii, Voprosy Khim.i Khim.Tekhnol., 1974, **35**, 39.
65. P.A.Sessa and H.A.McGee, Inorg.Chem., 1971, **10**, 2066.
66. I.V.Nikitin and V.Ya.Rosolovskii, Zhur.Fiz.Khim., 1974, **48**, 369 [Russ.J.Phys.Chem., 1974(2)].
67. F.Marsh, US P. 3 032 400/1962; Chem.Abs., 1962, **57**, 13 413.
68. P.J.Bassett and D.R.Lloyd, J.Chem.Soc., 1971, A, 3377.
69. W.B.Fox, J.S.McKenzie, and R.K.Vitek, US P. 3 306 834/1967; Chem.Abs., 1967, **67**, 55 834.
70. W.B.Fox, J.S.McKenzie, and R.Vitek, Inorg. Nuclear Chem.Letters, 1970, **6**, 177.
71. N.Vanderkooi, J.S.McKenzie, and W.B.Fox, J. Fluor.Chem., 1976, **7**, 415.
72. W.B.Fox, B.Sukornick, J.S.McKenzie, R.L.Sturtevant, A.F.Maxwell, and J.R.Holmes, J.Amer.Chem.Soc., 1970, **92**, 5240.
73. J.N.Wilson, Adv.Chem.Ser., 1966, **54**, 30.
74. W.E.Tolberg, R.T.Rewick, R.S.Stringham, and M.E.Hill, Inorg.Nuclear Chem.Letters, 1966, **2**, 79.
75. K.O.Christe, J.P.Guertin, and A.E.Pavlath, Inorg.Nuclear Chem.Letters, 1966, **2**, 83.
76. S.M.Sinel'nikov and V.Ya.Rosolovskii, Dokl.Akad. Nauk SSSR, 1970, **194**, 1341.
77. C.Gotzmer, US P. 3 981 756/1976.
78. D.Pilipovich, US P. 3 963 542/1976.
79. K.O.Christe, R.D.Wilson, and C.J.Schack, Inorg.Chem., 1977, **16**, 937.
80. H.R.Lubowitz and W.G.Gaskill, US P. 3 980 509/1976.
81. K.O.Christe, C.J.Schack, and R.D.Wilson, Inorg. Chem., 1976, **15**, 1275.
82. J.P.Guertin, K.O.Christe, and A.E.Pavlath, Inorg.Chem., 1966, **5**, 1921.
83. J.P.Guertin and A.E.Pavlath, US P. 3 503 719/1970; Chem.Abs., 1970, **72**, 123 534.
84. K.O.Christe, R.D.Wilson, and A.E.Axworthy, Inorg.Chem., 1973, **12**, 2478.
85. I.J.Solomon, U.S.Govt.Res.Devel.Rep., 1969, **69**, 62; Chem.Abs., 1969, **71**, 18 410.
86. C.T.Goetschel, V.A.Campanile, R.M.Curtis, K.R.Loos, C.D.Wagner, and J.N.Wilson, Inorg. Chem., 1972, **11**, 1696.
87. S.M.Sinel'nikov and V.Ya.Rosolovskii, USSR P.336 267/1970; Byull.Izobr., 1972, No.14, 72.
88. V.Ya.Rosolovskii, V.I.Nefedov, and S.M.Sinel'nikov, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1445.
89. V.Ya.Rosolovskii, Koord.Khim., 1978, **4**, 867.
90. S.P.Mishra, M.C.R.Symons, K.O.Christe, R.D.Wilson, and R.I.Wagner, Inorg.Chem., 1975, **14**, 1103.
91. K.O.Christe and I.B.Goldberg, Inorg.Chem., 1978, **17**, 759.
92. K.O.Christe, R.D.Wilson, and I.B.Goldberg, Inorg.Chem., 1979, **18**, 2572.
93. A.Smalc, K.Lutar, and J.Slivnik, J.Fluor.Chem., 1975, **6**, 287.
94. A.A.Artyukhov, V.N.Bezmel'nitsyn, Yu.V.Drobyshevskii, V.A.Legasov, V.B.Sokolov, and B.B.Chaivanov, "Tezisy Dokladov Pyatogo Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Proceedings of the Fifth All-Union Symposium on the Chemistry of Inorganic Fluorides), Dnepropetrovsk, 1978, p.36.
95. N.M.Matchuk, V.I.Tupikov, A.A.Malkova, and S.Ya.Pshezhetskii, Optika i Spektrosk., 1976, **40**, 14.
96. A.A.Streng, Canad.J.Chem., 1966, **44**, 1476.
97. I.V.Nikitin, A.V.Dudin, and V.Ya.Rosolovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 269.
98. I.V.Nikitin and A.V.Dudin, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 2127.
99. R.D.Coombe and R.K.Horne, J.Phys.Chem., 1979, **83**, 2805.
100. N.S.Nikolaev, V.F.Sukhoverkhov, Yu.D.Shishkov, and I.F.Alenchikova, "Khimiya Galoidnykh Soedinenii Ftora" (Chemistry of the Halogen Compounds of Fluorine), Izd.Nauka, Moscow, 1968.
101. D.F.Smith, Science, 1963, **141**, 1039.
102. W.Maya and H.F.Bauer, US P. 3 354 646/1967.

103. D.Pilipovich, W.Maya, E.A.Lawton, H.F.Bauer, D.F.Sheehan, N.N.Ogimachi, R.D.Wilson, F.C.Gunderloy, and V.E.Bedwell, Inorg.Chem., 1967, **6**, 1918.
104. K.O.Christe, Inorg.Chem., 1973, **12**, 1580.
105. S.M.Sinel'nikov and V.Ya.Rosolovskii, "Tizisy Dokladov Chetvertogo Vsesoyuznogo Simpoziuma po Khimii Neorganicheskikh Ftoridov" (Proceedings of the Fourth All-Union Symposium on the Chemistry of Inorganic Fluorides), Dushanbe, 1975, p.64.
106. R.J.Gillespie and G.J.Schrobilgen, Inorg.Chem., 1974, **13**, 1230.
107. D.Pilipovich, C.B.Lindahl, C.J.Schack, R.D.Wilson, and K.O.Christe, Inorg.Chem., 1972, **11**, 2189.
108. R.Bougon, J.Isabey, and P.Plurien, Compt.rend., 1970, C271, 1366.
109. K.O.Christe and C.J.Schack, Adv.Inorg.Chem. and Radiochem., 1976, **18**, 319.
110. Z.K.Nikitina, S.M.Sinel'nikov, and V.Ya.Rosolovskii, USSR P. 454166/1972; Byull.Izobr., 1974, No.47, p.37.
111. I.F.Isaev, K.A.Kazankii, and V.V.Mal'tsev, Atomnaya Energiya, 1968, **25**, 244.
112. I.F.Isaev, V.A.Legasov, Ya.R.Rakhimbabaev, V.D.Rusanov, and S.V.Tishin, "Tezisy Dokladov Vtorogo Vsesoyuznogo Simpoziuma po Plazmokhimii" (Proceedings of the Second All-Union Symposium on Plasma Chemistry), Izd.Zinatne, Riga, 1975, Vol.1, p.184.
113. J.Slivnik, A.Šmalc, K.Lutar, B.Žemva, and B.Frlec, J.Fluor.Chem., 1975, **5**, 273.
114. A.A.Artyukhov, V.A.Legasov, G.N.Makeev, B.M.Smirnov, and B.B.Chaivanov, Khim.Vys. Energii, 1976, **10**, 512.
115. A.A.Artyukhov, V.A.Legasov, G.N.Makeev, L.A.Palkina, B.M.Smirnov, and B.B.Chaivanov, Khim.Vys.Energii, 1977, **11**, 88.
116. A.A.Artyukhov, V.A.Legasov, G.N.Makeev, and B.B.Chaivanov, Khim.Vys.Energii, 1977, 11, 89.
117. V.N.Bezmel'nitsyn, V.A.Legasov, and B.B.Chaivanov, Dokl.Akad.Nauk SSSR, 1977, **235**, 96.
118. V.D.Klimov, V.A.Legasov, and S.S.Khoroshev, Zhur.Fiz.Khim., 1978, **52**, 1790 [Russ.J.Phys. Chem., 1978(7)].
119. S.M.Sinel'nikov, I.V.Nikitin, and V.Ya.Rosolovskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1968, 2806.
120. A.A.Malkova, V.I.Tupikov, I.V.Isakov, and V.Ya.Dudarev, Zhur.Neorg.Khim., 1974, **19**, 1729 [Russ.J.Inorg.Chem., 1974(7)].
121. V.A.Legasov and D.V.Orlinskii, "Proceedings of the Twelfth International Conference on Phenomena in Ionised Gases", Eindhoven, 1975, Part 1, p.205.
122. A.Smalc, K.Lutar, and J.Slivnik, J.Fluor.Chem., 1976, **8**, 95.
123. I.R.Beattie, A.German, H.E.Blayden, and S.B.Brumbach, J.Chem.Soc., Dalton Trans., 1975, 1659.
124. R.J.Lagow, L.L.Gerchman, R.A.Jacob, and J.A.Morrison, J.Amer.Chem.Soc., 1975, **97**, 518.
125. R.Eujen and R.J.Lagow, Inorg.Chem., 1975, **14**, 3128.
126. J.A.Morrison and R.J.Lagow, J.Inorg.Chem., 1977, **16**, 1823.
127. L.J.Turbini, R.E.Aikman, and R.J.Lagow, J.Amer. Chem.Soc., 1979, **101**, 5833.
128. M.Kaufman, Pure and Appl.Chem., 1976, **48**, 155.
129. J.L.Margrave, K.G.Sharp, and P.W.Wilson, Fortschr.chem.Forsch., 1972, **26**, 1.
130. E.Mathias and G.H.Miller, J.Phys.Chem., 1967, 71, 2671.
131. A.A.Kirpichnikova, I.V.Ermakova, and M.A.Englin, Zhur.Vses.Khim.Obshch.imeni Mendeleeva, 1977, **22**, 101.
132. J.P.Albrand, S.P.Anderson, H.Goldwhite, and L.Huff, Inorg.Chem., 1975, **14**, 570.
133. R.J.Lagow, L.A.Shimp, D.K.Lam, and R.F.Baddour, Inorg.Chem., 1972, **11**, 2568.
134. R.J.Lagow, R.F.Baddour, D.K.Lam, and L.A.Shimp, US P. 3904501/1975.
135. J.L.Margrave and P.W.Wilson, Acc.Chem.Res., 1971, **4**, 145.
136. K.G.Sharp and J.L.Margrave, J.Inorg.Nuclear Chem., 1971, **33**, 2813.
137. A.A.Kirpichnikova, V.G.Noskov, M.A.Englin, A.A.Chumakov, and A.N.Medvedev, Zhur.Vses. Khim.Obshch.imeni Mendeleeva, 1977, 22, 465.
138. W.C.Smith and V.A.Engelhardt, J.Amer.Chem.Soc., 1960, 82, 3838.
139. H.J.Emeléus and B.Tittle, J.Chem.Soc., 1963, 1644.
140. G.Bruno, P.Carpezzuto, and F.Cramarossa, J.Fluor. Chem., 1979, **14**, 115.
141. I.A.Tikhomirov, V.A.Klimenov, and V.A.Vlasov, "Tezisy Dokladov Tretego Vsesoyuznogo Simpoziuma po Plazmokhimii" (Proceedings of the Third All-Union Symposium on Plasma Chemistry), Moscow, 1979, 1, 136.
142. C.J.Mogab, A.C.Adams, and D.L.Flamm, J.Appl. Phys., 1978, **49**, 3796.
143. Yu.I.Dikarev, V.I.Esin, and V.F.Synorov, "Tezisy Dokladov Tretego Vsesoyuznogo Simpoziuma po Plazmokhimii" (Proceedings of the Third All-Union Symposium on Plasma Chemistry), Moscow, 1979, Vol.1, p.299.
144. F.J.Lovas and D.R.Johnson, J.Chem.Phys., 1973, 59, 2347.
145. Yu.N.Tumanov and N.P.Galkin, Radiokhimiya, 1976, **18**, 714.

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