RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

March 1967

U. D. C. 546.16

PERCHLORYL FLUORIDE: PRODUCTION, PHYSICAL PROPERTIES, AND REACTIONS

V. M. Khutoretskii, L. V. Okhlobystina, and A. A. Fainzil'berg

CONTENTS

I. Introduction 145

II. Production of perchloryl fluoride 145

III. Physicochemical properties of perchloryl fluoride 146

IV. Reactions of perchloryl fluoride 147

1. Reactions with inorganic compounds 148

2. Reactions with organic compounds 148

V. Uses 154

I. INTRODUCTION

The rapid development of investigations into the preparation and chemistry of perchloryl fluoride $FClO_3$† has made it available not only for study, but also for practical applications.

The marked difference between the exceptionally stable $FClO_3$ and the other unstable oxide fluorides of chlorine has made it of special interest. The high symmetry of its molecule and the great similarity in electronegativities of fluorine and the ClO_3 group explain the stability of perchloryl fluoride and its chemical behaviour as a two-centre electrophilic substance. It is still the only reagent for perchlorylation (introduction of the ClO_3 group) at carbon in organic compounds and at the same time it exhibits the properties of a selective fluorinating agent. The oxidative dimerisation and oxofluorination which can be effected with the aid of $FClO_3$ are reactions of independent interest. The fact that the perchloryl fluoride molecule is made up of atoms of the most electropositive elements determines its behaviour as a strong oxidant.

The available literature on the properties of this compound has been very inadequately surveyed. Brief reviews in Japanese[1] and Chinese[2] have been published, but these dealt with only a small part of the literature. A Russian review[3] which recently appeared was principally devoted to the selective fluorination of steroids.

In the present review we aim to cover as completely as possible the literature on the production, physical properties, and reactions of perchloryl fluoride in the period from 1950 to mid-1965.

II. PRODUCTION OF PERCHLORYL FLUORIDE

Perchloryl fluoride was first obtained by Engelbrecht and Atzwanger[4] in 1952 by the electrolysis of a saturated solution of sodium perchlorate in anhydrous hydrogen fluoride, with a current efficiency of 10%.

A year earlier, Bode and Klesper, who investigated the action of elemental fluorine on potassium chlorate, reported the production of a compound of composition $FClO_3$,[5] which in reality was a mixture of chloryl fluoride $FClO_2$, chlorine, and perchloryl fluoride[6,7]; the last can be isolated in yields of up to 45%.[8] The fluorination was carried out in the solid phase using fluorine diluted with nitrogen at temperatures up to 50°C. The use of efficient cooling (-25°C) and strict control of temperature in working with undiluted fluorine, supplied at a low rate, allowed the yield of $FClO_3$ to be increased to 60%.[9]

† Better written ClO_3F (Ed. of Translation).

In addition to perchloryl fluoride, several gaseous products are formed in the reaction of potassium chlorate with fluorine: Cl_2, $FClO_2$, O_2, Cl_2O_6, and FCl.[8,9] To free $FClO_3$ from impurities it is passed through alkaline solutions of reductants and then condensed at liquid oxygen temperature. This method seemed so effective (after the treatment the proportion of impurities did not exceed 1.5%) that it was used without significant changes in all subsequent work on the preparation of perchloryl fluoride.

Note that both methods (electrochemical and the fluorination of chlorates by fluorine) have several drawbacks: the need to work with special metal apparatus, the difficulty of temperature control in solid-phase fluorination, low yields, etc.

Replacement of elemental fluorine by other fluorinating agents (ClF_3, BrF_3, SbF_5) did not give positive results: the yield of perchloryl fluoride was too low, and the main reaction products with potassium chlorate were $FClO_2$ and Cl_2.[8] Only the use of perchlorates instead of chlorates led to the development of convenient methods of making $FClO_3$.

When potassium perchlorate is heated (70–120°) in an excess of antimony(V) fluoride, perchloryl fluoride is formed in 50% yield. Other metal perchlorates (sodium, barium, magnesium) or perchloric acid can be used in this reaction[10].

Of other reactions, that of perchlorates with fluorosulphonic acid has been studied in greatest detail[11-17]. This method of obtaining $FClO_3$, which was proposed in 1956 by Barth-Wehrenalp[11], is now evidently the simplest and most convenient. Solutions of potassium perchlorate in fluorosulphonic acid are heated at various temperatures. Liberation of perchloryl fluoride starts at 50°, the reaction goes to completion with the temperature gradually rising to 85° or 110°. The yields of perchloryl fluoride vary within the range 50–80%[11-13]. If necessary the fluorosulphonic acid can be regenerated for reuse[12]. The great convenience of the method is that the reaction can be carried out in the usual glass apparatus; moreover the initial substances are available and cheap.

Unfortunately the mechanism of the process has been little studied. The initial suggestion[11] that the compound $(ClO_2)_2S_3O_{10}$ was formed as an intermediate was disproved after a more critical consideration[15,16]. It is now thought more probable that there is an acid–base reaction, expressed by the equation:

$$3\,HSO_3F + KClO_4 \rightleftarrows ClO_3^+ + 3\,SO_3F^- + H_3O^+ + K^+,$$

and the formation of $FClO_3$ is considered to be the result of the thermal decomposition of this equilibrium mixture[15].

With the aim of increasing the yield of perchloryl fluoride in the reaction of potassium perchlorate with fluorosulphonic acid the influence of various fluorine-containing additions was studied: BF_3, HF, SbF_3, and other metal fluorides[17]. Thus, the addition of 5–25 parts SbF_3 per 100 parts fluorosulphonic acid increases the yield of $FClO_3$ to 90% and over. Addition of BF_3 and HF also increases the yield to 85%. Unfortunately, the introduction of these has a bad effect on other aspects of the reaction: SbF_3 hinders the regeneration of fluorosulphonic acid, and BF_3 and HF require pressure for carrying out the reaction. Zinc, aluminium, silver, and lead fluorides, on the other hand, decrease the yield of perchloryl fluoride[17].

The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulphonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used and their additional purification is not necessary; unlike all the previous methods the preparation of perchloryl fluoride by this method can be carried out at room temperature. At high temperature (100–135°) the reaction time is 1–10 min in all, which allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches 98% and over, air and carbon dioxide being present as trace impurities[18,19].

III. PHYSICOCHEMICAL PROPERTIES OF PERCHLORYL FLUORIDE

The physical and physicochemical properties of perchloryl fluoride have now been studied rather fully (see Table 1).

Under ordinary conditions perchloryl fluoride is a colourless gas with a characteristic sweetish odour. On cooling to -46.8° it condenses to a colourless liquid, which solidifies at -147.75°.

Unlike other compounds of fluorine with oxygen and chlorine (F_2O, $FClO_2$, $FClO_4$, ClF_3, etc.), perchloryl fluoride exhibits exceptional thermal and hydrolytic stability. Dry perchloryl fluoride is almost stable on heating to 500°[20] and is not hydrolysed in the slightest by water even on heating to 250–300°.[8] Perchloryl fluoride does not explode on detonation, but it forms explosive mixtures with certain organic substances[20], which must be taken into account in working with it.

Addition of an inhibitor is not needed for storing $FClO_3$ in either the liquid or the gaseous states. Dry perchloryl fluoride does not corrode most common metals[20]. It does not react with stainless steel, copper, or aluminium[21,22]; of organic materials, Kel-F oil — poly(chlorotrifluoroethylene)[22] — and ethylene–propylene rubber[23] are chemically rather stable towards it. Moist perchloryl fluoride reacts appreciably with vacuum grease and with mercury[24].

TABLE 1.

Physicochemical properties of perchloryl fluoride	Reference
Boiling point −46.68°C	24
Melting point −147.75°C	24
Density of liquid at 20°C 1.434 g ml^{-1} *	27
Critical parameters:	
temperature 95.17°C	27
pressure 53.0 atm	27
density 0.637 g ml^{-1}	8
molar volume 161 cm^3	8
Trouton's constant 21.97	8
Heat of vaporisation	
at boiling point 4.6 kcal $mole^{-1}$	24,27
at 25°C 3.5 kcal $mole^{-1}$	29
Viscosity of liquid:	
at −80°C 0.62 cP	29
at 0°C 0.219 cP	
at +60°C 0.139 cP	
Heat capacity of the liquid at 50°C 0.29 cal g^{-1} deg^{-1}	29
Density of the solid at −190°C 2.19 g cm^{-3}	31
Heat of fusion 916 cal $mole^{-1}$	24
Surface tension at −55.6° 21.3 dyn cm^{-1}	28
Ratio C_p/C_v at 24°C 1.12±0.01	32
Entropy at 25° 66.51 e.u.	24

* It appears that the authors have used an equation for the liquid density as a function of temperature obtained in the range 131°K to 234°K[27] and has used this to give the figure quoted for density at 20°C! (Ed. of Translation).

Perchloryl fluoride is sparingly soluble in water, rather more soluble in organic solvents. Under ordinary conditions (25°, 760 mmHg) its solubility varies within the range 1.5–5.5 g litre^{-1}. The highest solubility is in dioxan, nitrobenzene, and dimethyl formamide [1,25,26].

Empirical equations have been obtained for the temperature dependence of vapour pressure [8,24,27], the density of the liquid [8,27], and the viscosity of the liquid [28]. Detailed information has been published on the heat capacity of liquid perchloryl fluoride at various temperatures [24,29,30], its surface tension [28], and viscosity [28,29].

Structure and Spectra

A compound of composition $FClO_3$ can have one of two structures:



(A) (B)

On the basis of the vibrational spectra, perchloryl fluoride was ascribed structure (B), having the chlorine as central atom and symmetry of type C_{3v}. [33,34] In fact, on comparing structures (A) and (B), the first should have the structure of a triangular pyramid and the second a tetrahedron with the chlorine atom at the centre. Structure (A) could not have symmetry of a type higher than C_S, whereas structure (B) corresponds to a symmetry of type C_{3v}. Accordingly, structure (A) would correspond to the presence of nine main bands active in the infrared region, and structure (B) to six bands. In the observed spectrum of $FClO_3$ there are only six main frequencies (see Table 2), which supports structure (B). The absence of a microwave spectrum for perchloryl fluoride is also considered as confirmation of the C_{3v} model [35].

The infrared spectrum of $FClO_3$ has also appeared in other papers [8,36]. The assignment of the frequencies, made on the basis of a comparison with the spectra of ClO_4^- and FCl, [33] was confirmed by investigation of the Raman spectra [37,38] (see Table 2) and of the high-resolution infrared spectrum in the 525–625 cm^{-1} region [34].

Some correlations with the infrared spectra of perchloryl fluoride have also been made. Thus, Sharp [39] notes a significant similarity in the infrared spectra of $FClO_3$ and FSO_3^-, which is isoelectronic with it; Robinson [40] found a linear relation between the frequencies of the symmetric and asymmetric stretching vibrations of the $-PO_2$ and $-ClO_2$ groups which is also suitable for many oxygen ligands.

TABLE 2. Vibrational spectra of perchloryl fluoride*.

Raman spectrum (Ref.37)	Infrared spectrum (Ref.33)	Assignment of frequencies
410 v.s.	405	ν_6 (e) rocking
549 s.	549	ν_3 (a_1) deformation ClO_3
587 m.	589	ν_5 (e) deformation ClO_3
695—724 m.	704 }	ν_2 (a_1) stretching $^{37}Cl-F$
	714 }	ν_2 (a_1) stretching $^{35}Cl-F$
1061 v.s.	1061	ν_1 (a_1) stretching Cl–O
1312 w.	1315	ν_4 (e) stretching Cl–O

* s strong; vs very strong; m medium; w weak.

The values of the frequencies here depend regularly on the electronegativity of the groups connected to the central atom.

The dipole moment of perchloryl fluoride is very low [35]; its accurate value of 0.023 ± 0.003 D was determined by using specially sensitive apparatus [41].

From measurements of the vapour pressure, heats of fusion and vaporisation, and the phase transformation temperatures, the entropy of perchloryl fluoride as an ideal gas at the boiling point has been calculated [24] to be 60.17 e.u. From the table of thermodynamic properties [42] this quantity was found to be 62.59 e.u. (interpolation). For a crystal with disordered arrangement of the F and O atoms at 0°K the difference in these quantities should be $R \ln 4 = 2.75$ e.u. The fact that the observed difference is slightly less than this value shows that there is a high degree of disorder in the arrangement of the fluorine and oxygen atoms in the perchloryl fluoride crystal [24].

Tallman and coworkers [31,43] give X-ray diffraction data and the density of crystalline perchloryl fluoride at liquid air temperature. From these data the authors assume that crystalline perchloryl fluoride has a tetragonal cell ($a = b = 7.66$ Å, $c = 5.31$ Å). The ^{19}F-NMR spectra of perchloryl fluoride have been discussed [44–46]. According to the interpretations in References 44 and 46 the observed spectra are the sum of $F^{35}ClO_3$ and $F^{37}ClO_3$ spectra, in each of which there is spin–spin interaction of the fluorine nucleus with the nucleus of the corresponding Cl isotope (both isotopes have spin $I = \frac{3}{2}$). The F–Cl spin–spin interaction which is observed extremely rarely in spectra here becomes observable, apparently owing to the low rate of relaxation of the chlorine nucleus, which is in turn due to the highly symmetrical environment of the chlorine atom (that is, the anomalously low constant of the quadrupole interaction of the chlorine nuclei). The very high chemical shift (320 p.p.m. to lower fields relative to CF_3CO_2H lines) shows the extremely low negative charge on the fluorine, in other words, the high degree of covalency of the F–Cl bond in the $FClO_3$ molecule. The fact that the electronegativities of fluorine and the ClO_3 group are close to one another is also confirmed by the absence of a dipole moment from $FClO_3$. [41]

The mass spectrum of perchloryl fluoride has been studied [47–49]. The potentials for the appearance and the relative intensities of the negative [47,49] and positive [49] ions in the mass spectrum have been determined. On the basis of these potentials hypothetical values have been advanced for the ionisation energies of the radicals obtained in the breakdown of the $FClO_3$ molecule, and the heat of formation of perchloryl fluoride has been estimated to be -5.3 ± 4 kcal × × mole^{-1} (in good agreement with the -5.12 ± 0.68 kcal × × mole^{-1} from another study [50]) and the dissociation energies of the bonds to be $D_{(O_3Cl-F)} = 60$ kcal mole^{-1} and $D_{av(Cl-O)} = 57$ kcal mole^{-1}. [49]

IV. REACTIONS OF PERCHLORYL FLUORIDE

As noted above, perchloryl fluoride exhibits high thermal stability and considerable stability to hydrolysis. Appreciable thermal decomposition of perchloryl fluoride is observed only at temperatures of ~500°C. Gatti and coworkers [51,52] studied the kinetics of thermal decomposition of perchloryl fluoride at 470–500°C over a wide pressure interval (5–1000 mmHg) by the equation

$$2FClO_3 \rightarrow 2ClF + 3O_2.$$

They found that the reaction is unimolecular and completely homogeneous (in quartz); the activation energy is 58.4 ± 2 kcal mole^{-1}.[52] The application of a dimensionless molecular transfer equation, based on similarity theory, to chemical kinetics, in particular for the example of thermal decomposition of perchloryl fluoride, allowed the main kinetic characteristics of the process (rate and activation energy) to be obtained without employing any assumptions about the mechanism[53].

1. REACTIONS WITH INORGANIC COMPOUNDS

Perchloryl fluoride does not react with dilute aqueous solutions of alkalis or thiosulphate, nor with solid alkalis[8,13].

Even at 250–300° the hydrolysis of $FClO_3$ is very slow. Quantitative hydrolysis is brought about by concentrated alkali solutions at the same temperature, according to the equation:

$$FClO_3 + 2\,NaOH \rightarrow NaClO_4 + NaF + H_2O.$$

However, in an alcoholic solution of potassium hydroxide perchloryl fluoride is readily split at 25°C with the formation of a precipitate of $KClO_4$, and KF is left in solution. This reaction can be used for the quantitative determination of $FClO_3$.[1]

The reaction of $FClO_3$ with sodium and potassium starts only at ~300°C, although it proceeds rather vigorously[8].

All these results led initially to perchloryl fluoride's being considered a chemically inert substance but, as appeared subsequently, this does not correspond with reality. Perchloryl fluoride is capable of reacting vigorously with several inorganic and organic compounds at moderate temperatures and even on cooling below 0°C.

Perchloryl fluoride reacts rather easily with liquid ammonia or its aqueous solutions[8,54] by the equation:

$$FClO_3 + 3\,NH_3 \rightarrow NH_4F + NH_4NHClO_3.$$

The reaction takes place quantitatively in a few hours. Sodium amide greatly accelerates the reaction in liquid ammonia. From the ammonium salt perchloryl amide, which could not be isolated pure, the silver, caesium, and potassium salts have been obtained: $AgNHClO_3$, $CsNHClO_3$, Cs_2NClO_3, $KNHClO_3$, K_2NClO_3, which are derivatives of the unstable amide of perchloric acid, $H_2N{-}ClO_3$. These salts, especially in the dry form, are sensitive to impact, friction, and the action of a flame.

Perchloryl fluoride oxidises potassium iodide. The reaction proceeds quantitatively on shaking for 4–5 h a solution of KI in 0.1 *N* acid with perchloryl fluoride[8]:

$$FClO_3 + 8\,I^- + 6\,H^+ \rightarrow Cl^- + F^- + 4\,I_2 + 3\,H_2O.$$

In his review Nakanishi[1], in referring to published data[55], states that oxidations involving $FClO_3$ depend to a considerable extent on the reaction temperature, the pH of the medium, and the concentration of the reagents. At high temperatures many reactions proceed explosively. For example, a mixture of $FClO_3$ and H_2S in certain proportions explodes at 150°. With a dilute mixture the rate of reaction at this temperature is low and the reaction is:

$$3\,FClO_3 + 4\,H_2S \rightarrow 4\,SO_2 + 3\,HF + 3\,HCl + H_2O.$$

Reaction with hydrogen chloride in the gas phase at 200–300° proceeds with the formation of chlorine by the equation:

$$FClO_3 + 7\,HCl \rightarrow HF + 4\,Cl_2 + 3\,H_2O.$$

2. REACTIONS WITH ORGANIC COMPOUNDS

In reactions with organic compounds $FClO_3$ behaves as either an oxidant or a two-centre electrophile which, depending upon the conditions, can be used for the introduction of either fluorine or the ClO_3 group.

Fluorination

The reaction of perchloryl fluoride which has been studied best is the fluorination of organic compounds at a carbon having a mobile hydrogen atom. These include compounds with a methylene or methine group activated by one or more electronegative groupings (ketone, alkoxycarbonyl, aldehyde, nitrile, etc.). A necessary condition for the fluorination is the presence of an equimolar amount of a base (usually an alkali metal alkoxide) or the introduction into the reaction of a previously prepared metal derivative of the compound being fluorinated.

Carbonyl compounds. Inman and coworkers[56,57] effected the first fluorinations of compounds with an active methylene group by the action of perchloryl fluoride. They found that ethyl and phenyl malonates react smoothly with perchloryl fluoride in the presence of bases, giving the corresponding monofluoro-substituted esters with yields of over 70%:

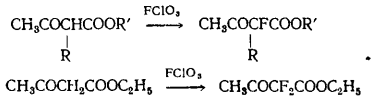
$$RCH(COOC_2H_5)_2 \xrightarrow{FClO_3} RCF(COOC_2H_5)_2.$$

The fluorination of malonic esters proper does not stop at the stage of the monofluoro-derivative but leads to the exclusive formation of the difluoromalonate even when there is insufficient base‡. The authors' explanation for this is that the monofluoromalonate ester, which is evidently a stronger acid§ than malonic, undergoes the fluorination more rapidly.

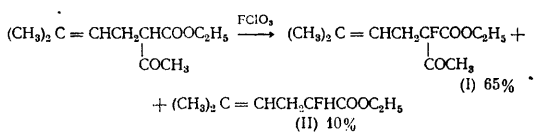
‡ After this review had been written there appeared a paper by Gershon and coworkers[124] describing a more detailed investigation of the action of perchloryl fluoride on malonic ester. It was found that in this reaction in addition to the difluoromalonate there are several other products, including the monofluoromalonate. The qualitative and quantitative composition of the mixture depends on the solvent and the ratio of the reactants.

§ We do not think that this conclusion of the authors is sufficiently well founded. It was recently established[125,126], for fluoronitroalkanes, that the introduction of a fluorine atom in the α position to an electron-acceptor substituent (the nitro-group) does not increase, but, on the contrary, greatly lowers the acidity of the compound. In accordance with this, fluoromalonic ester should be a weaker, not a stronger, acid than malonic ester. On the other hand the ease of fluorination is evidently determined more by the nucleophilic nature of the compound being fluorinated than by its acidity.

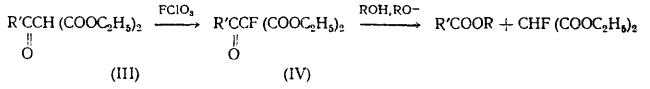
Perchloryl fluoride reacts readily with β-keto-esters [57-59], α-substituted keto-esters giving the monofluoro-derivatives [58,59], but acetacetic ester giving the difluoro-derivative exclusively [57]:



A side-reaction here is the removal of the acetyl group, which is facilitated by an excess of the base and raising the temperature. Thus, in the fluorination of the ethyl ester of 2-acetyl-5-methylhex-4-enoic acid two compounds were isolated: the expected fluorination product (I) and its diacetylated analogue (II) [58]:

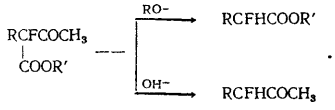


The acetyl group is even more readily detached from fluorinated acetyl diesters. Thus, in the presence of bases fluorination of esters of type (II) leads to the formation of a deacetylated compound as the main product — a monofluoromalonic ester — and only a little of fluorination product (IV) [59]:

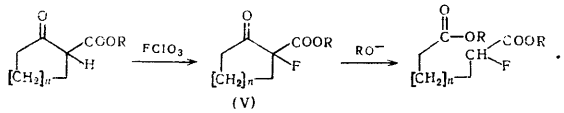


In the fluorination of esters of tricarboxylic acids an ethyloxalyl group can be removed [60,61].

The property of the α-fluoro-α-alkyl-β-keto-esters to lose an acetyl group under the action of bases or an alkoxycarbonyl group in OH-catalysed hydrolysis was used for a directed synthesis of several esters of α-fluorocarboxylic acids [59] and α-fluorinated ketones [58]:

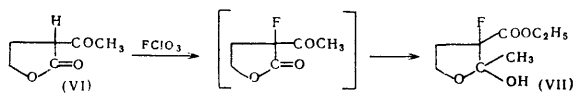


Cyclic β-keto-esters react with perchloryl fluoride like the acyclic esters [62], but not all the fluoro-compounds which are obtained (V) are stable:

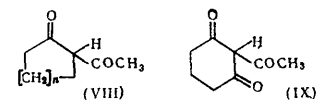


Thus the fluorination product (V; n = 1) could not be isolated, as it underwent a series of changes, leading to ring opening. The most stable fluorination products were compounds with larger rings (V; n = 2, 3) or bicyclic systems. Under the action of alkaline agents compounds of type (V) are readily hydrolysed and decarboxylated, forming cyclic α-fluoroketones [62,63].

On reaction with perchloryl fluoride, lactones of type (VI) also give unstable fluoro-derivatives which undergo a series of transformations under the conditions of the reaction [59,64]. Thus, the final result of the fluorination of lactone (VI) was the formation of (VII) [59]:

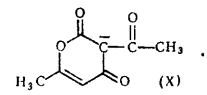


Cyclic β-diketones (VIII) and triketones (IX) also react with $FClO_3$; the regularity in the formation of fluorination products for them is the same as for cyclic β-keto-esters — ring opening, deacetylation [62]:

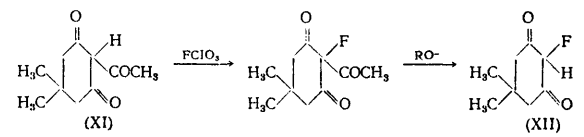


The less nucleophilic nature of the anions of tricarbonyl compounds (in comparison with dicarbonyl compounds) leads to a decrease in the reactivity towards perchloryl fluoride, and the reaction is slow.

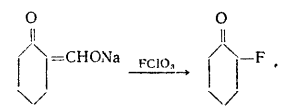
Anions which are still more resonance-stabilised such as (X), generally do not react with perchloryl fluoride [62].



In the example of tricarbonyl compounds reacting with $FClO_3$ mention must be made of the side-reaction, which can occur in the fluorination of other compounds. When the reaction leads to the formation of compound (XII), which is a stronger acid than the original compound (XI), the former can displace the latter from its salts. Then the compound being fluorinated (XI) is partly recovered unchanged, which leads to a fall in the yield of the desired reaction product:

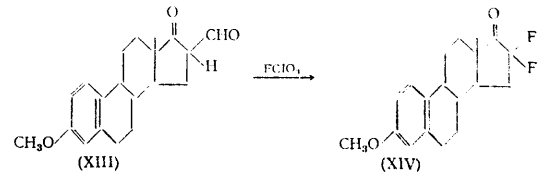


α-Formylated cyclic ketones behave analogously to α-acetylketones in reaction with perchloryl fluoride: the fluorination is accompanied by loss of the formyl group and sometimes the difluoro-derivative is formed. Fluorination of sodium 2-oxocyclohexylidenemethoxide leads to the formation of 2-fluorocyclohexanone in 40% yield [65]:



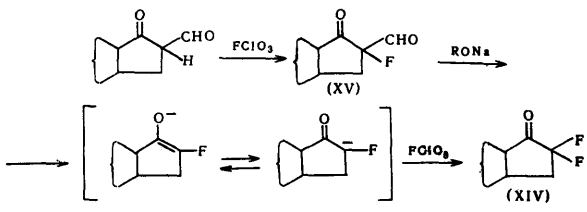
Dipole moment measurements have established the equatorial conformation of the fluorine in the 2-fluorocyclohexanone obtained. This compound serves as a standard for finding the conformation of the α-fluoroketones of the steroidal series.

The fluorination of the α-formylated cyclic ketones has been used successfully to obtain fluorinated analogues of certain steroids¶. Thus, the 3-methyl ether of 16-formyloestrone (XIII) reacts with $FClO_3$ in t-butyl alcohol to give at once the 3-methyl ester of 16,16-difluoro-oestrone (XIV) in the presence of a large excess of sodium butoxide [67]:



¶ Methods of obtaining fluorosteroids have been reviewed in detail. [66]

The authors assume that the monofluoroformyl derivative (XV) is formed as an intermediate, which subsequently reacts with the base and perchloryl fluoride to give the $\alpha\alpha$-difluoroketone (XIV):

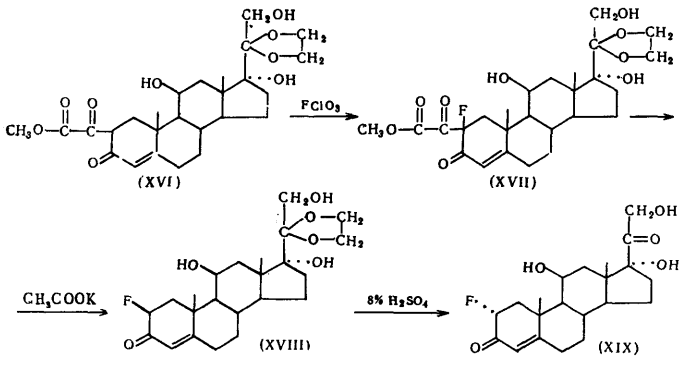


Proof of the proposed scheme was given by the isolation of the monofluoroketone (XV) corresponding to the first stage of the reaction[68].

Monofluoroketones of the androstane series were obtained by an analogous reaction in benzene; the 2-formyl--2-fluorosteroids formed on fluorination were treated with a base to remove the formyl group. For example: 2-fluorotestosterone, 2α-fluoro-17β-hydroxyandrostan--3-one, etc. were obtained in this way[69].

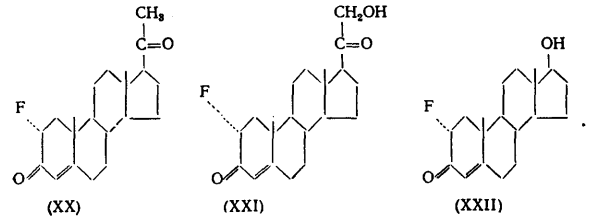
The introduction of fluorine into positions 6α 9α, and 12α of hydrocortisone leads to highly active glucocorticoids. The reaction of $FClO_3$ with the sodium salts of the enol forms of β-dicarbonyl compounds is very convenient for obtaining fluorinated steroidal hormones. This method evidently allows fluorine to be introduced into any methylene or methyl group of the steroid capable of alkylation with the formation of a β-dicarbonyl system. In turn the acylation is conveniently effected by the introduction of an alkoxalyl group[70,71] which is readily detached after fluorination.

For the synthesis of 2α-fluorohydrocortisone, 20-ethyleneketalhydrocortisone was treated with methyl oxalate and sodium methoxide in benzene. The ethyleneketal was taken to prevent methoxalylation at position 21. The 2-methoxalylhydrocortisone-20-ethyleneketal (XVI) which was obtained reacted with perchloryl fluoride[72,73]:



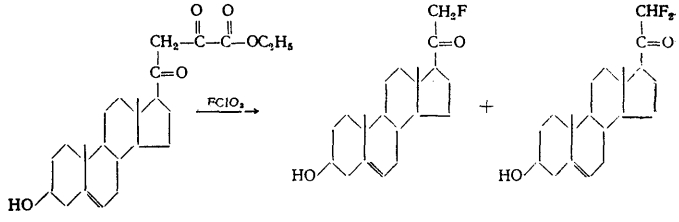
After removal of the methoxalyl group from (XVII) the substance (XVIII) was obtained in 43% yield. The yield of the desired 2α-fluorohydrocortisone (XIX) from (XVIII) was 73%.

2α-fluoroprogesterone (XX) was obtained analogously (44% yield calculated on the initial ethyleneketal), 2α-fluorodeoxycorticosterone (XXI) (25%), and 2α-fluorotestosterone (XXII) (20%)[72]:



A series of fluoro-substituted steroids containing fluorine in positions 2 and 21 has been obtained by the reaction of $FClO_3$ with alkoxalylated steroids[25,72-76]. Most authors consider the conformation of the 2-fluoro-3-keto-derivatives of steroids which are obtained to be equatorial (2α) from measurements of the dipole moments and by analogy of the optical rotatory dispersion curves with those for other halogeno-substituted compounds for which the conformation has been established[65,72,74,78].

Both monofluoro- and difluoro-derivatives were obtained by the fluorination of the 21-ethoxylalyl derivatives of 20-keto-steroids[72]:



An interesting example of fluorination by perchloryl fluoride has been described[77]. It was shown that steroids with the $-\overset{\overset{O}{\|}}{C}-CF_2H$ group are capable of being fluorinated by perchloryl fluoride in the presence of bases, giving a trifluoro-derivative with the $-\overset{\overset{O}{\|}}{C}-CF_3$ group.

Fluorination of tetracyclines with perchloryl fluoride has also been described[79].

Nitriles and nitro-compounds. Compounds with a methylene group activated not only by carbonyl groups but also by other electronegative substituents (the nitrile group and the nitro-group) are fluorinated by perchloryl fluoride.

Substituted malonodinitriles[80] and phenylacetonitriles[81] give fluorinated products with $FClO_3$ in the presence of bases. It has been proposed to use as bases the alkali metals, and their hydroxides, hydrides, amides, and alkoxides[81]:

$$RC(CN)_2H \xrightarrow{FClO_3} RC(CN)_2F.$$

The sodium salts of secondary nitro-compounds (2-nitropropane, 2-nitrobutane, and nitrocyclohexane) are fluorinated by perchloryl fluoride in methanol, forming a fluoronitro-compound in 36-42% yield — Eqn. (1). The fluorination is accompanied by side-reactions: by oxidation and by oxidative dimerisation, as a result of which ketones — Eqn. (2) — and vicinal dinitro-compounds — Eqn. (3) — are formed[82]:

$$R_2C{=}NO_2^- + FClO_3 \rightarrow R_2CFNO_2 + ClO_3^- \quad (1)$$

$$R_2C{=}NO_2^- + FClO_3 \rightarrow R_2C{=}O + [HNO_2] + HClO_3 + F^- \quad (2)$$

$$2\,R_2C{=}NO_2^- + FClO_3 \rightarrow \underset{\displaystyle NO_2\ NO_2}{R_2C{-}CR_2} + F^- + ClO_3 \quad (3)$$

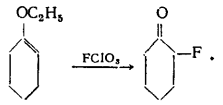
In the fluorination of primary nitro-compounds appreciable quantities of fluoronitroalkanes (3–5%) could not be obtained; mainly oxidation products are formed here — aldehydes (32–55%). Salts of such nitro-compounds as nitromalonic ester, α-nitro-α-phenyl acetophenone, etc., which have other electronegative substituents in the α position to the nitro-group are converted into the corresponding α-fluoronitro-compounds in high yields (80%)[83].

Oxidative dimerisation, which is observed as a side-reaction in the fluorination of nitroalkanes, is sometimes the main reaction. Thus, in an attempt to fluorinate acylamidomalonates with perchloryl fluoride in the presence of sodium ethoxide oxidative dimerisation products were obtained exclusively[84]:

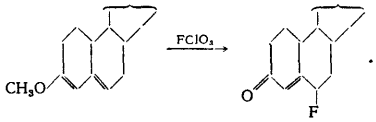
$$2\,RNH{-}CH(COOC_2H_5)_2 \xrightarrow{FClO_3} RNH{-}C(C_2H_5OOC)_2{-}C(C_2H_5OOC)_2{-}NHR$$

where R = HCO, CH_3CO.

Ethers of enols readily react with perchloryl fluoride in pyridine, forming α-fluoro-ketones in high yields. Thus 2-fluorocyclohexanone was obtained from 1-ethoxycyclohexene; the reaction with steroids having the same structural fragment — an ethoxy-group at a double bond — proceeds analogously[77]:



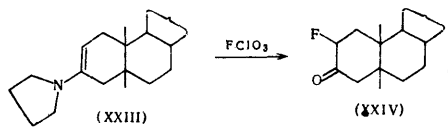
In the presence of two conjugated double bonds the fluorine enters position 6 of the steroid nucleus[77,85]:



Esters of enols (for example, acetates) react like ethers; the reaction takes place in an inert organic solvent, on adding weakly basic nucleophilic agents (water, pyridine)[86,87]. The reactivity of enol acetates with two conjugated double bonds is higher than with one double bond[88]; the latter react much more slowly[89,90].

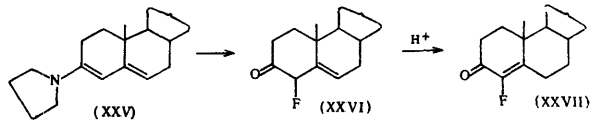
Enamines and enamides. The replacement of oxygen by nitrogen in steroid derivatives, that is, the use of enamides (acetylated enamines) instead of enol acetates considerably facilitates the fluorination. 3β-acetoxy-17-acetaminoandrosta-5,16-diene reacts with $FClO_3$ in pyridine at room temperature within 3 min, the yield of 3β-acetoxy-16α-fluoroandrost-5-en-17-one reaching 70% (against 45% after 20 h from the corresponding enol acetate)[90,91]. A sharp rise in reactivity of enamides compared with enol acetates agrees with the greater ability of the nitrogen atom to give electrons to a double bond, which should facilitate reaction with the electrophilic fluoride of the perchloryl fluoride[90,91].

Enamines are rather reactive in relation to $FClO_3$ but often give a mixture of different reaction products in ratios which depend on the fluorination conditions. Pyrrolidylenamine of cholestan-3-one (XXIII) gives 2α-fluorocholestan-3-one (XXIV) in 72% yield after passing $FClO_3$ into a benzene solution of (XXIII) for 30 s:[92]



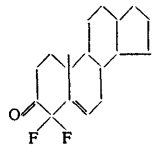
(XXIII) (XXIV)

Pyrrolidylenamines of steroids with two conjugated double bonds (XXV) in methanol and dimethylformamide react with $FClO_3$ to form monofluoro-substituted compounds of general formula (XXVI), the isomerisation of which in strongly acid medium leads to (XXVII)[93,94]:



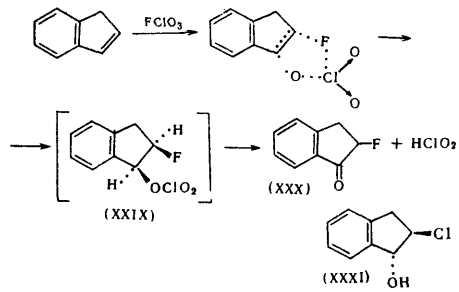
(XXV) (XXVI) (XXVII)

In ether enamines of type (XXV) give mainly 4,4-difluoro-3-keto-Δ^5-steroids (XXVIII)[95,96]:



(XXVIII)

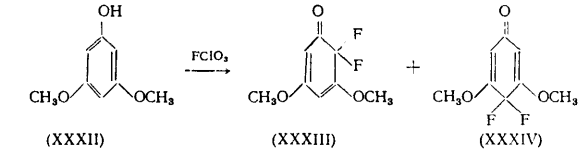
Oxofluorination. Compounds having a cyclic double bond conjugated with an aromatic nucleus, are capable of entering with perchloryl fluoride into the reaction termed oxofluorination, the final result of which is the formation of α-fluoroketones. For example, indene reacts in this way. In this reaction $FClO_3$ acts as a two-centre electrophile which attacks the 2–3 double bond of indene. As a result of this, according to the authors' hypothesis[97], a *cis*-fluoro-chlorate (XXIX) is formed as an intermediate, which is converted into the final α-fluoro-ketone (XXX) by loss of the acid $HClO_2$. This acid apparently takes part in the formation of the *trans*-2-chloroindanol (XXXI) which is isolated from the mixture in considerable quantity:



(XXIX) (XXX) (XXXI)

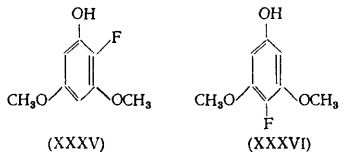
The products of oxofluorination are also formed by the action of perchloryl fluoride on the ethers of enols and enamines, as already mentioned above.

Phenols react with $FClO_3$, forming products of *C*-fluorination in which the fluorine usually enters the *ortho*- and *para*-positions. The molecule acquires a quinoidal structure. When perchloryl fluoride acts on 3,5-dimethoxyphenol (XXXII) in pyridine or dimethylformamide a mixture of two isomeric difluoro-compounds (XXXIII) and (XXXIV) is formed:



(XXXII) (XXXIII) (XXXIV)

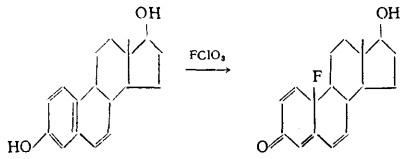
Paper chromatography of the reaction mixture allows the fluorophenols (XXXV) and (XXXVI) to be detected; they may be precursors of the final compounds (XXXIII) and (XXXIV) respectively:



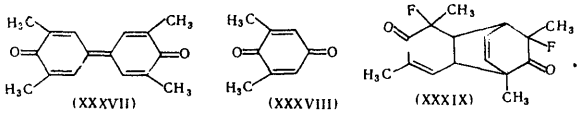
(XXXV) (XXXVI)

Reactions with 2- and 4-chloro-3,5-dimethoxyphenols give predominantly *gem*-chlorofluorodienones, the reduction of which with zinc in acetic acid leads to fluorophenols [98,99].

10β-fluorinated steroids are formed by the action of $FClO_3$ on steroidal phenols. In dimethylformamide the yields are higher than in dioxan [100,101]:

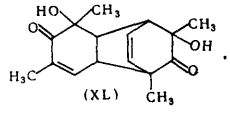


The reaction of perchloryl fluoride with phenols was studied in greater detail for 2,6-dimethylphenol [102]. As a result of the reaction of sodium 2,6-dimethylphenate a mixture of products was obtained, the composition of which depended on the solvent used. In media of low dielectric strength (pentane, dioxan, toluene) quinones (XXXVII), (XXXVIII), and a fluorination product in the form of a dimer (XXXIX) are formed:



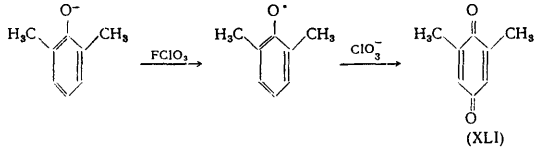
(XXXVII) (XXXVIII) (XXXIX)

In polar solvents (ethanol, dimethylformamide) instead of the dimer (XXXIX) a dimer of analogous structure (XL) is obtained:



(XL)

The authors explain the formation of quinones by the oxidation of the phenate anion to a radical and its subsequent conversion:



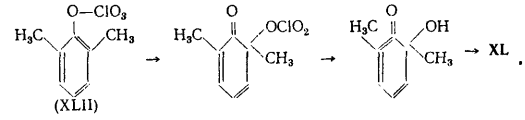
(XLI)

2,6-dimethylphenol itself in toluene does not react with perchloryl fluoride; in dimethyl formamide the reaction is very slow and a mixture of dimethylquinone (XLI) and 2,6-dimethyl-4-chlorophenol is formed. The formation of the latter can be explained by the action on 2,6-dimethylformamide of hypochlorous acid, which in turn is formed at the end of a sequence of redox changes:

$$FClO_3 \rightarrow ClO_3 \rightarrow HClO_2 \rightarrow OClH.$$

The definite influence of the medium on the formation of dimers (XXXIX) and (XL) prompted the authors [102] to suggest that these compounds are the products of the attack of a two-centre nucleophile — dimethylphenate — on perchloryl fluoride, which plays the part of a two-centre electrophile.

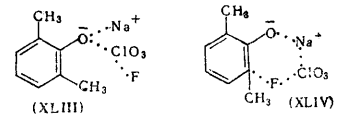
As a result of the attack by oxygen of the phenate ion on the chlorine of the perchloryl fluoride and subsequent intramolecular oxidative disproportionation of compound (XLII), the dimer (XL) is formed:



(XLII)

Were the nucleophilic centre the *ortho*-carbon atom of the phenate ion, then its attack by fluorine would lead finally to the dimer (XXXIX). The reaction of perchloryl fluoride at the carbon or oxygen of the phenate can be compared with the known *O*- or *C*-alkylation of phenates.

The transition state can be either (XLIII) or (XLIV):



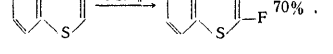
(XLIII) (XLIV)

The greater solvation of the cation favours the transition state (XLIII) which leads to the intermediate formation of the ester of perchloric acid (XLII) and then to the dimer (XL). Qualitatively similar results are observed in the alkylation in polar media, when, in accordance with the Ingold hypothesis, the phenate anion reacts at the oxygen and the ion pair at the carbon [103]. Here the more strongly solvating medium facilitates a shift in the equilibrium to the side of an increase in the number of ions (including the phenate anion), which leads, finally, to an increase in the yield of the dimer (XL).

On the other hand the quasicyclic structure of the transition state (XLIV) favours the loss of $NaClO_3$ owing to the electrostatic attraction between the Na^+ group and the ClO_3 group. The gain in energy of the C–F bond compared with F–Cl is also the driving force of the process.

The fact that carbanions usually react with perchloryl fluoride at the fluorine but heteroatomic anions (and amines) at the chlorine, is explained by the authors in the following way: *C*-fluorination is energetically quite a favourable process, whereas the low polarisability (in comparison with the mesomeric carbanions) of the heteroatomic anion and the high electron density at the hetero-atom leads to the repulsion of the *p*-orbital of fluorine and of the hetero-atom (nitrogen or oxygen) [102].

As yet the only example of the fluorination of heterocyclic compounds has been described by Schuetz and coworkers [104]. It was shown that in the presence of butyl-lithium thiophen and some of its derivatives are fluorinated by perchloryl fluoride in position 2:



Under these conditions phenyl-lithium and naphthyl-lithium give an extremely small quantity of fluoro-derivatives. With phenyl-lithium perchlorylbenzene could be isolated from the products of the reaction.

Oxidative fluorination. An interesting, but little studied reaction of $FClO_3$ is that with oximes. Perchloryl fluoride in pyridine is capable not only of fluorinating oximes at carbon, but also of simultaneously oxidising the oxime group to a nitro-group. Since, however, very few substances have been studied it is therefore uncertain how general this reaction is (so-called oxidative fluorination).

The dimethyl ester of oximinomalonic acid forms with perchloryl fluoride in dimethylformamide an oxidative fluorination product in 70% yield:

$$(CH_3OOC)_2C{=}NOK \xrightarrow{FClO_3} (CH_3OOC)_2C\begin{matrix}NO_2\\F\end{matrix}.$$

In the reaction potassium chlorate and chloride are formed. It is interesting that chloronitromalonic ester was isolated as a side-product, the quantity of which rose as the chloride ion accumulated[83]. In this respect the reaction differs from fluorination at an "active methylene" group, which is not sensitive to the presence of foreign ions[57].

The reaction could not be extended to other oximes, for example, the ethyl ester of α-oximino-β-ketobutyric acid† and the ethyl ester of oximinocyanoacetic acid. Some oximes under the action of $FClO_3$ undergo a Beckmann rearrangement of the second kind. Thus, on treating the sodium salt of α-benzil monoxime (XLV) with perchloryl fluoride it forms a mixture of benzil monoxime benzoate (XLVI) and benzonitrile:

$$\underset{\text{(XLV)}}{2\,C_6H_5\overset{O}{\overset{\|}{C}}-\overset{N-O}{\overset{\|}{C}}-C_6H_5} \xrightarrow{FClO_3} \underset{\text{(XLVI)}}{C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{N-O-\overset{O}{\overset{\|}{C}}-C_6H_5}{\overset{\|}{C}}-C_6H_5} + C_6H_5CN.$$

Oximes which do not contain electronegative substituents (acetophenone, benzophenone) are converted into the original ketones under the action of perchloryl fluoride[83].

The possibility of using perchloryl fluoride as an oxidant in analysis has been studied[105]. It was shown that in non-aqueous media at room temperature the aldehyde group is very stable to the action of perchloryl fluoride but the amino- and mercapto-groups undergo complex redox conversions.

Perchlorylation

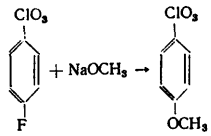
In the presence of a Friedel–Crafts catalyst (usually $AlCl_3$) perchloryl fluoride reacts with aromatic compounds by a type of electrophilic substitution, giving perchlorylaromatic compounds, for example, perchlorylbenzene[106,107]. In the absence of a catalyst the reaction does not take place, but at the same time a complex of the catalyst with perchloryl fluoride was not obtained in the absence of the reagent. Possibly the reaction proceeds through a transition state in which all three components are combined. By analogy with the electrophilic acylation of benzene by Friedel–Crafts, the authors propose the following mechanism for the reaction[107]:

$$FClO_3 + AlCl_3 \rightarrow [FClO_3 \cdot AlCl_3] \rightarrow ClO_3^+ AlFCl_3^-$$
$$C_6H_6 + ClO_3^+ \rightarrow C_6H_5ClO_3 + H^+$$
$$H^+ + AlFCl_3^- \rightarrow HCl\uparrow + AlFCl_2.$$

† The author probably means sodioethyloximinoacetoacetate (Ed. of Translation).

Benzene derivatives (fluorobenzene, phenol, 1,2,3-trifluorobenzene, xylene, etc.) react with perchloryl fluoride. However, the perchlorylation of nitrobenzene and some other aromatic compounds with electronegative substituents could not be carried out.

Perchlorylaromatic compounds are stable in vacuum and steam distillation but can be detonated under severe impact or by a high temperature. They are stable in acid or neutral media but are hydrolysed in strongly alkaline solutions, forming the phenate and chlorate ions. The reaction of halogeno-substituted perchlorylaromatic compounds with alkoxides (and some other reactions with nucleophiles) takes place with retention of the perchloryl group in the nucleus[108], for example:



Reductants such as lithium tetrahydroaluminate, tin(II) chloride in hydrochloric acid, and zinc in hydrochloric acid, do not reduce the ClO_3 group[107], but on a palladium catalyst perchlorylaromatic compounds are readily hydrogenated according to the equation[109]:

$$R-C_6H_4-ClO_3 + 4\,H_2 \xrightarrow[CH_3COOH]{Pd} RC_6H_5 + HCl + 3\,H_2O.$$

A large number of derivatives are obtained from perchlorylbenzene by the usual methods; they include 4-chloro-, 4-methylthio-, and pentachloro-perchlorylbenzene and 3-perchlorylanilinium chloride. Perchlorylbenzene and its homologues are sulphonated by concentrated sulphuric acid and are nitrated in the *meta*-position by sulphuric–nitric mixture. Azo-, azoxy-, and hydrazo-3-perchlorylbenzenes are also obtained. The infrared spectra of substituted perchlorylbenzenes have been studied[106,107].

Only brief mention has been made of the perchlorylation of alkoxide anions by perchloryl fluoride[56]. With sodium trifluoroethoxide in trifluoroethanol $FClO_3$ gives trifluoroethyl perchlorate and sodium fluoride:

$$F_3CCH_2ONa + FClO_3 \rightarrow F_3CCH_2OClO_3 + NaF.$$

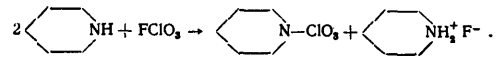
With the less acidic alcohols the reaction does not stop at the stage of the formation of an ester of perchloric acid, but proceeds further by the equation:

$$RO^- \xrightarrow{FClO_3} ROClO_3 \xrightarrow{RONa} ROR + NaClO_4.$$

Thus, sodium ethoxide in ethanol reacts with perchloryl fluoride to give diethyl ether and sodium perchlorate[56].

As already noted, perchloryl fluoride and ammonia give a mixture of ammonium fluoride and the ammonium salt of perchloramide[8,54]. Attempts to carry out an analogous reaction with amines did not lead to the desired result. Perchloryl fluoride reacts with pure amines, usually explosively or forming a complex mixture of oxidation products, usually of the anil type. Aminolysis of perchloryl fluoride by aniline, phenylhydrazine, isopropylamine, isobutylamine, etc. led to the formation of spontaneously explosive solid or liquid substances of unknown structure[110].

Only recently[111] an amine was perchlorylated at the nitrogen. On passing $FClO_3$ into an aqueous solution of piperidine, *N*-perchlorylpiperidine was obtained in 70% yield. This is an unstable liquid, readily hydrolysed by alkalis and highly explosive:



A review has been published[112] part of which is devoted to a consideration of the preparation and properties of perchlorylorganic compounds.

Toxicity

With reference to preliminary tests made on animals, Engelbrecht and Atzwanger[8] characterise perchloryl fluoride as "moderately toxic" 7–8 degrees in Carpenter and coworkers' classification, and give numerical values for LC_{50}: 2000–4000 parts per million in exposure for 4 h. The toxicity of perchloryl fluoride is close to the toxicity of chlorine but without its irritating action[20]. Its odour is detectable in a concentration of 10 parts per million, which is considerably below the permissible concentration on prolonged action. Gall[114] mentions that the toxicity of perchloryl fluoride is low and it does not damage the skin. It was also noted[115] that monkeys can breathe air containing 40 parts per million perchloryl fluoride for a long time but at 200 parts per million slight toxic action is observed.

V. USES

As perchloryl fluoride is a comparatively new substance its possible practical uses are still insufficiently studied. The prospects of using perchloryl fluoride as an oxidant have been considered more than any others. The spectra of flames of some fuel gases with perchloryl fluoride as oxidant have been studied[116] and the rate of flame in mixtures of methane with air on adding perchloryl fluoride has been measured[117]. Schmauch and Servass[115,118] note that the flame of the combination $H_2 + FClO_3$ is readily controlled, has a low background, and can be used with success as a source of excitation in flame photometry.

As an oxidant for rocket propellents[29] liquid perchloryl fluoride in combination with dimethylhydrazine or hydrazine has a specific impulse of 274 s (combustion chamber pressure 42 atm), whereas liquid oxygen with the American fuel JP-4 gives 272 s. In a hybrid, solid–liquid system, perchloryl fluoride gives the same specific impulse as dinitrogen tetroxide, that is, 246 s.[119]

The use of perchloryl fluoride as an oxidant for the high-temperature cutting of metals has been proposed[120].

The possibility of using perchloryl fluoride in other fields is at the discussion stage. There are several patents on its use as a heat transfer medium in refrigeration[121], and as an insecticide–fungicide[122]. The polymerisation of ethylene in the presence of perchloryl fluoride under a pressure of hundreds of atmospheres and a temperature of the order of 200°C has been reported[123].

Thanks to the ability to intensively absorb slow electrons[47] perchloryl fluoride can find application as a gaseous insulator, the dielectric properties of which are better than those of SF_6 and hardly deteriorate on irradiation by γ-rays[21].

Perchloryl fluoride is at present the only agent for obtaining perchlorylaromatic compounds. The latter can find a use for obtaining explosive substances, dyes, and pharmaceutical preparations (3-perchlorylacetanilide, and 4-fluoroperchlorylbenzene exhibit pharmacological potential)[2,106].

1. S. Nakanishi, J. Jap. Chem., 13, 864 (1959).
2. Ching-Yung Tao, Hua Hsueh Tung Pao, No. 5, 44 (1962)
3. Yu. A. Titov, I. G. Reshetova, and A. A. Akhrem, RIMIOS, No. 15 (1966).
4. A. Engelbrecht and A. Atzwanger, Monatsh., 83, 1087 (1952).
5. H. Bode and E. Klesper, Z. anorg. Chem., 266, 275 (1951).
6. H. Bode and E. Klesper, Angew. Chem., 66, 605 (1954).
7. A. Engelbrecht, Angew. Chem., 66, 442 (1954).
8. A. Engelbrecht and H. Atzwanger, J. Inorg. Nuclear Chem., 2, 348 (1956).
9. J. Sicre and H. Schumacher, Angew. Chem., 69, 266 (1957).
10. A. Engelbrecht, U. S. P. 2 942 947 (28th June 1960); Chem. Abs., 54, 21 681b (1960).
11. G. Barth-Wehrenalp, J. Inorg. Nuclear Chem., 2, 266 (1956).
12. G. Barth-Wehrenalp, U. S. P. 2 942 948 (28th June 1960); Chem. Abs., 54, 21 681c (1960).
13. W. Lalande, German P. 1 026 285 (10th March 1958); Chem. Abs., 54, 20 117i (1960).
14. W. Lalande, U. S. P. 2 982 617 (2nd May 1961); Chem. Abs., 55, 16 916i (1961).
15. A. Woolf, J. Inorg. Nuclear Chem., 3, 250 (1956).
16. G. Barth-Wehrenalp, J. Inorg. Nuclear Chem., 4, 374 (1957).
17. H. Dess, U. S. P. 2 982 618 (2nd May 1961); Chem. Abs., 55, 16 927b (1961).
18. G. Barth-Wehrenalp and H. Mandell, German P. 1 076 640 (5th November 1958); Chem. Abs., 56, 5631i (1962).
19. G. Barth-Wehrenalp and H. Mandell, U. S. P. 2 942 949 (28th June 1960); Chem. Abs., 54, 21 681d (1960).
20. Chem. Eng. News, 38, 62 (1960).
21. J. Gall, U. S. P. 3 038 955 (29th November 1956); Chem. Abs., 8 066c (1962).
22. W. Lalande and J. Gall, U. S. P. 2 998 388 (19th December 1956); Chem. Abs., 57, 16 365c (1962).
23. J. Green, N. Levine, and R. Keller, Ind. Eng. Chem., Prod. Res. Develop., 2, 126 (1963).
24. J. Koehler and W. Giauque, J. Amer. Chem. Soc., 80, 2659 (1958).
25. B. Magerlein, J. Pike, R. Jackson, G. Vandenberg, and F. Kagan, J. Org. Chem., 29, 2982 (1964).
26. A. Nathan, B. Magerlein, and J. Hogg, J. Org. Chem., 24, 1517 (1959).
27. R. Jarry, J. Phys. Chem., 61, 498 (1957).
28. J. Simkin and R. Jarry, J. Phys. Chem., 61, 503 (1957).
29. J. Gall, "Space and Aeronautics, 1959", Research and Development Handbook, 1959–1960, p. 5.
30. R. Jarry and J. Fritz, Chem. Eng. Data Ser., 3, 34 (1958).
31. R. Tallman, D. Wampler, and J. L. Margrave, J. Inorg. Nuclear Chem., 21, 38 (1961).
32. J. L. Margrave and R. Wendt, J. Chem. Phys., 31, 857 (1959).
33. D. Lide and D. Mann, J. Chem. Phys., 25, 1128 (1956).
34. R. Madden and W. Benedict, J. Chem. Phys., 25, 594 (1956).
35. D. Lide and D. Mann, J. Chem. Phys., 25, 595 (1956).
36. E. Smith, F. Steinbach, and K. Beu, U. S. Atomic Energy Commission Report, GAT-T-687 (1959); Nucl. Sci. Abs., 13, No. 20 883 (1959); Chem. Abs., 54, 20 617i (1960).
37. F. Powell and E. Lippincott, J. Chem. Phys., 32, 1883 (1960).
38. J. Dunlop and E. Jones, Spectroscopia Mol., 9, No. 98, 32 (1960).
39. D. W. A. Sharp, J. Chem. Soc., 3761 (1957).
40. E. Robinson, Canad. J. Chem., 41, 173 (1963).
41. A. Maryott and S. Kryder, J. Chem. Phys., 27, 1221 (1957).
42. D. Lide and D. Mann, U. S. Nat. Bur. Stand. Report No. 4399 (1st November 1955); Cited in Ref. 24.
43. R. Tallman, Diss. Abs., 20, 4293 (1960).
44. S. Brownstein, Canad. J. Chem., 38, 1597 (1960).
45. H. Agahigian, A. Gray, and G. Vickers, Canad. J. Chem., 40, 157 (1962).

46. J. Bacon, R. J. Gillespie, and J. Quail, Canad. J. Chem., 41, 3063 (1963).
47. W. Hickman and D. Berg, J. Chem. Phys., 29, 517 (1958).
48. R. Reese, V. Dibeler, and F. Mohler, J. Res. Nat. Bur. Stand., 57, 367 (1957).
49. V. Dibeler, R. Reese, and D. Mann, J. Chem. Phys., 27, 176 (1957).
50. C. Neugebauer and J. L. Margrave, J. Amer. Chem. Soc., 79, 1338 (1957).
51. R. Gatti, J. Sicre, and H. Schumacher, Angew. Chem., 69, 638 (1957).
52. R. Gatti, J. Sicre, and H. Schumacher, Z. phys. Chem. (Frankfurt), 23, 164 (1960).
53. A.G. Usmanov and R. I. Magarra, Zhur. Fiz. Khim., 36, 2680 (1962) [Russ. J. Phys. Chem., 1454 (1962)].
54. H. Mandell and G. Barth-Wehrenalp, J. Inorg. Nuclear Chem., 12, 90 (1959).
55. Booklet DC-1819, Pennsalt Chemicals Corp., Commercial Development Dept., Philadelphia, cited in Ref. 1.
56. C. Inman, E. Tyczkowski, R. Oesterling, and F. Scott, Experientia, 14, 355 (1958).
57. C. Inman, R. Oesterling, and E. Tyczkowski, J. Amer. Chem. Soc., 80, 6533 (1958).
58. H. Machleidt, Annalen, 667, 24 (1963).
59. H. Machleidt, Annalen, 676, 66 (1964).
60. L. Gottwald and E. Kun, J. Org. Chem., 30, 877 (1965).
61. F. Dean and F. Pattison, Canad. J. Chem., 41, 1833 (1963).
62. H. Machleidt and V. Hartmann, Annalen, 679, 9 (1964).
63. H. Lange and M. Lipp, Naturwiss., 47, 397 (1960).
64. H. Machleidt and R. Wessendorf, Annalen, 674, 1 (1964).
65. A. Kende, Tetrahedron Letters, No. 14, 13 (1959).
66. A. A. Akhrem, I. G. Reshetova, and Yu. A. Titov, Uspekhi Khim., 34, 2171 (1965) [Russ. Chem. Rev., 926 (1965)].
67. C. H. Robinson, N. F. Bruce, E. P. Oliveto, S. Tolksdorf, S. Steinberg, and P. L. Perlman, J. Amer. Chem. Soc., 82, 5256 (1960).
68. C. H. Robinson, N. F. Bruce, and E. P. Oliveto, J. Org. Chem., 28, 975 (1963).
69. J. Edwards and H. Ringold, J. Amer. Chem. Soc., 81, 5262 (1959).
70. H. Ruschig, Ber., 88, 878 (1955).
71. G. Allen and M. Weiss, J. Amer. Chem. Soc., 81, 4968 (1959).
72. H. Kissman, A. Small, and M. Weiss, J. Amer. Chem. Soc., 82, 2312 (1960).
73. H. Kissman, A. Small, and M. Weiss, J. Amer. Chem. Soc., 81, 1262 (1959).
74. C. Holmlund, L. Feldman, H. Kissman, and M. Weiss, J. Org. Chem., 27, 2122 (1962).
75. B. P. 907 813 (8th September 1958); Chem. Abs., 58, 8009c (1963).
76. A. Nathan, J. Babcock, and J. Hogg, J. Amer. Chem. Soc., 82, 1436 (1960).
77. S. Nakanishi, K. Morita, and E. Jensen, J. Amer. Chem. Soc., 81, 5259 (1959).
78. N. Allinger, H. Blatter, M. Darooge, and L. Freiberg, J. Org. Chem., 26, 2550 (1961).
79. H. Renhard, R. Blackwood, and C. Stephens, J. Amer. Chem. Soc., 83, 2775 (1961).
80. A. Josey, U. S. P. 3 114 763 (20th January 1960); Chem. Abs., 60, 7918g (1964).
81. B. P. 865 321 (12th April 1961); Chem. Abs., 56, 331g (1962).
82. H. Schechter and E. Roberson, J. Org. Chem., 25, 175 (1960).
83. J. Freeman, J. Amer. Chem. Soc., 82, 3869 (1960).
84. H. Gershon and A. Scala, J. Org. Chem., 27, 463 (1962).
85. B. J. Magerlein, F. H. Lincoln, R. D. Birkenmeyer, and F. Kagan, Chem. and Ind., 2050 (1961).
86. V. Bogert and B. Bloom, U. S. P. 2 961 441 (22nd November 1960); Chem. Abs., 56, 528e, 6061h (1962).
87. B. Bloom, V. Bogert, and R. Pinson, Chem. and Ind., 1317 (1959
88. G. Allen and N. Austin, J. Org. Chem., 26, 5245 (1961).
89. E. Jensen, in "Abstracts of Papers Presented at the 138th Meeting of American Chemical Society, New York, 11th–16th September, 1960", p. 25M.
90. S. Nakanishi and E. Jensen, J. Org. Chem., 27, 702 (1962).
91. S. Nakanishi, J. Med. Chem., 7, 108 (1963).
92. R. Gabbard and E. Jensen, J. Org. Chem., 23, 1406 (1958).
93. R. Joly and J. Warnant, Bull. Soc. chim. France, 569 (1961).
94. R. Joly, J. Warnant, and A. Guillemette, French P. 1 260 066 (21st March 1960); Chem. Abs., 57, 2291c (1962).
95. S. Nakanishi. R. Morgan, and E. Jensen, Chem. and Ind., 1136 (1960).
96. S. Nakanishi, Steriods, 2, 765 (1963).
97. M. Neeman and Y. Osawa, J. Amer. Chem. Soc., 85, 232 (1963).
98. D. Taub, Chem. and Ind., 558 (1962).
99. D. Taub, C. Kuo, and N. Wendler, Chem. and Ind., 557 (1962).
100. J. Mills, J. Barrera, E. Olivares, and H. Garcia, J. Amer. Chem. Soc., 82, 588 (1960).
101. J. Mills, J. Amer. Chem. Soc., 81, 5515 (1959).
102. A. Kende and P. MacGregor, J. Amer. Chem. Soc., 83, 4197 (1961).
103. C. K. Ingold, Ann. Reports, 142 (1926).
104. R. D. Schuetz, D. D. Taft, J. P. O'Brien, J. L. Shea, and H. M. Mork, J. Org. Chem., 28, 1420 (1963).
105. R. Shoho, Diss. Abs., 23, 3100 (1963).
106. C. Inman, R. Oesterling, and E. Tyczkowski, U. S. P. 3 076 853 (21st June 1962). Chem. Abs., 59, 7428d (1963).
107. C. Inman, R. Oesterling, and E. Tyczkowski, J. Amer. Chem. Soc., 80, 5286 (1958).
108. F. Scott, U. S. P. 3 047 589 (31st July 1962); Chem. Abs., 58, 1397a (1963).
109. F. Scott and R. Oesterling, J. Org. Chem., 25, 1688 (1960).
110. F. Scott, R. Oesterling, E. Tyczkowski, and C. Inman, Chem. and Ind., 528 (1960).
111. D. Gardner, R. Helitzer, and C. Mackley, J. Org. Chem., 29, 3738 (1964).
112. G. N. Dorofeenko, S. V. Krivun, V. I. Dulenko, and Yu. A. Zhdanov, Uspekhi Khim., 34, 219 (1965) [Russ. Chem. Rev., 88 (1965)].
113. C. Carpenter, H. Smyth, and U. Pozzani, J. Ind. Hyg. Toxical, 31, 343 (1949).
114. J. Gall, ARS J., 29, 95 (1959).
115. G. Schmauch and E. Servass, Appl. Spectroscopy, 12, 98 (1958).
116. R. Lodwig and J. Margrave, Combustion and Flame, 3, 147 (1959).
117. C. Halpern, J. Res. Nat. Bur. Stand., 65A, 513 (1961).
118. G. Schmauch and E. Servass, Analyt. Chem., 30, 1160 (1958).
119. F. Hendel and E. Cavecche, Chem. Eng., 67, 93 (1960).
120. J. Gall, U. S. P. 3 066 058 (27th November 1962); Chem. Abs., 58, 6510a (1963).
121. W. Lalande and J. Gall, U. S. P. 2 998 388 (19th December 1956); Chem. Abs., 57, 16 365c (1962).
122. M. Goebel, U. S. P. 2 913 366 (17th November 1959); Chem. Abs., 54, 2649d (1960).
123. N. Hardwike, U. S. P. 2 947 738 (2nd August 1960); Chem. Abs., 54, 25 999h (1960).
124. H. Gershon, J. Renwick, W. Wynn, and R. D'Ascoli, J. Org. Chem., 31, 916 (1966).
125. V. I. Slovetskii, L. V. Okhlobystina, A. A. Fainzil'berg, A. I Ivanov, L. I. Biryukova, and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2063 (1965).
126. I. L. Knunyants, L. S. German, and I. N. Rozhkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1062 (1966).

Zelinskii Institute of Inorganic Chemistry,
Academy of Sciences of the USSR, Moscow