RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

November 1971

U. D. C. 546.07 + 546.163.1

Oxygen Fluorides and Dioxygenyl Compounds

I.V.Nikitin and V.Ya.Rosolovskii

The review considers the methods of preparation, structures, and properties of oxygen fluorides and dioxygenyl compounds which are genetically related to them.
The bibliography includes 124 references.

CONTENTS

I.	Introduction	889
II.	Oxygen fluorides	889
III.	Dioxygenyl compounds	896

I. INTRODUCTION

The oxygen compounds of the halogens constitute one of the groups of compounds of the most electronegative elements. Substances of this kind are oxidants with a high energy store, which are capable of releasing their chemical energy under certain conditions either instantaneously or at a controlled rate. Compounds of fluorine and oxygen are of special interest in this sense, since they comprise light electronegative atoms.

The chemical bond between oxygen and the halogens is covalent. The names adopted for the binary compounds of oxygen and halogens—"oxygen fluorides" and "chlorine, bromine, and iodine oxides"—reflect the electronegativity of the elements and are consistent with the rules of the International Union of Pure and Applied Chemistry (IUPAC).

This review deals with oxygen fluorides, the methods for their preparation, and their physical properties, structures, and reactions. The existing reviews[1-3] no longer embrace the entire accumulated experimental data. The authors of the present review do not claim an exhaustive presentation of the subject, their aim being to examine mainly studies published after the extensive review by Streng[1].

One of the most important properties of oxygen fluorides is their capacity to react with fluorine-containing Lewis acids forming dioxygenyl salts. Dioxygenyl hexafluoroplatinate, the first compound of the O_2^+ cation (obtained by Hartlett[4]), preceded and simulated the synthesis of valence compounds of xenon[5]. These studies had a significant influence on the development of modern refined inorganic syntheses. Dioxygenyl compounds are considered in a separate section of the present review.

II. OXYGEN FLUORIDES

1. Oxygen Difluoride

Oxygen difluoride has been known since 1927.[6] A widely employed method for the separation of OF_2 is based on the reaction of gaseous fluorine with a dilute aqueous solution of alkali[1,7]:

$$2F_2 + 2NaOH\ (KOH) \rightarrow OF_2 + 2NaF\ (KF) + H_2O\ .$$

Oxygen difluoride is also obtained by the electrolysis of hydrogen fluoride containing added water and an alkali metal fluoride[1,8]. Recently the reaction of fluorine with water in the presence of an alkali metal (Na, K, and Cs) fluoride was proposed as a method for the preparation of OF_2.[9] The synthesis is carried out in a glass apparatus where the HF and SiF_4 formed combine with the metal fluoride and do not contaminate the desired product, the yield of which reaches 80%.

Oxygen difluoride is thermally stable up to 200–250°C. It melts at −224°C, the yellow liquid boiling at −145°C; the vapour pressure of OF_2 is 1 mmHg at −196°C and 11 mmHg at −183°C.[1] Probably the most reliable value of the standard enthalpy of formation, $\Delta H^\circ_{f298}[OF_{2(gas)}] = 5.86 \pm 0.38$ kcal mole^{-1}, has been obtained[10] by measuring the heat of combustion of hydrogen in OF_2. The average thermochemical energy of the O–F bond in the OF_2 molecule is 45.7 kcal mole^{-1}.[10] The dissociation energy of the first O–F bond is less than the dissociation energy of the second bond; for example, $D(F-OF) \simeq 42.7$ and $D(OF) \simeq 48.3$ kcal mole^{-1} have been quoted[11].

The geometrical parameters of the OF_2 molecule have been determined by microwave spectroscopy[12]: $r(O-F) = 1.390$ Å and $\angle FOF = 104°16'$, differing somewhat from $r(O-F) = 1.412$ Å and $\angle FOF = 103°10'$ obtained by Pierce et al.[13] The infrared spectrum of gaseous OF_2 contains three intense bands corresponding to three normal vibrations: 928 (symmetrical stretching), 461 (deformation), and 831 cm^{-1} (antisymmetric stretching) and a number of weak absorptions—overtones and compound frequencies: 1281, 1648, 1728, 1740, 1840, 2188, 2455, 2643 cm^{-1}.

Oxygen difluoride is an effective fluorinating agent, somewhat inferior in reactivity to elemental fluorine[15]. In systems subjected to the action of an electric discharge or radiation, oxygen difluoride both fluorinates and oxidises. The reaction of OF_2 with unsaturated nitrogen fluorides in an electric discharge results in the formation of nitrogen trifluoride, oxide fluorides, and oxide[16]. By exposing oxygen difluoride and NF_3 to an electric discharge, it is possible to obtain trifluoroamine oxide[17,18]. A photochemical reaction of OF_2 with chlorine trifluoride has been used to synthesise chlorine oxide trifluoride $ClOF_3$.[19] When ionising radiation acts[20] on a mixture of NF_3 and OF_2 at −196°C, O_2F_2 and N_2O_4 are formed. XeF_2 and KrF_2 have been obtained by the photochemical fluorination of xenon[21] and krypton[22]. By heating a mixture of xenon and oxygen difluoride to 400°C or passing a mixture of the reactions through a discharge, XeF_4 and xenon oxide fluorides have been synthesised[1]. Oxygen difluoride does not react with liquid chlorine, or with gaseous chlorine at a moderate temperature, but in an electric discharge at low temperatures a reaction leading to the formation of ClF, ClO_2, and ClO_2F takes place[16].

The primary stage in the thermal reactions of oxygen difluoride with nitrogen dioxide[23] and tetrafluorohydrazine[24] is the abstraction of a fluorine atom from the OF_2 molecule:

$$(N_2O_4 \rightleftarrows 2NO_2)\ NO_2 + FOF = FNO_2 + OF,$$
$$(N_2F_4 \rightleftarrows 2NF_2)\ NF_2 + FOF = NF_3 + OF\ . \qquad (*)$$

The activation energy for reaction (*) is 22.5 kcal mole^{-1}. We may note for comparison that the activation energy for the reaction

$$NF_2 + F_2 = NF_3 + F$$

is only 9.7 kcal mole^{-1}.[25] The reaction of oxygen difluoride with tetrafluorohydrazine,

$$2N_2F_4 + OF_2 = FNO + 3NF_3\ ,$$

gives rise to nitrosyl fluoride, which does not react with oxygen difluoride below 170°C.[24]

Certain reactions involving oxygen difluoride may be regarded as addition to the second reactant of a fluorine atom and an OF radical—fragments derived from OF_2. When radiation at a wavelength of 3650 Å was allowed to act on a mixture of OF_2 and SO_3 at room temperature, fluoroperoxy-sulphuryl fluoride FSO_2OOF was obtained[26,27]. If the radiation includes quanta the energy of which is sufficient for the excitation of sulphur trioxide, then FSO_2OOF is formed in trace amounts and the main reaction products are pyrosulphuryl fluoride and sulphuryl fluoride[28]. The fact that the OF group in fluoroperoxysulphuryl fluoride originates from oxygen difluoride was demonstrated[29] in a study of the reaction of OF_2 and SO_3 by a tracer atom method, the products being analysed by ^{17}O NMR. The photochemical reaction of oxygen difluoride with peroxydisulphuryl difluoride[28] yields FSO_2OOF and FSO_3F. The reaction probably takes place as follows:

$$(1)\ F_2S_2O_6 \rightleftarrows FSO_3 + FSO_3,\ (2)\ OF_2 \rightarrow F + OF,$$
$$(3)\ FSO_3 + F = FSO_3F, \qquad (4)\ FSO_3 + OF = FSO_2OOF\ .$$

The photochemical reaction of OF_2 with sulphur dioxide gave pyrosulphuryl fluoride and sulphuryl fluoride[28], whereas on heating OF_2 and SO_2 to 300–500°C sulphuryl and thionyl fluorides are formed[30].

The reaction of oxygen difluoride with primary amines[31] leads to the formation of nitroso-compounds or oximes, for example nitrosocyclopropane has been obtained by the oxidation of cyclopropylamine at −42°C. It is believed that the interaction of OF_2 with amines can be described in terms of the following mechanism[31]:

$$RNH_2 + OF_2 \rightarrow [\overset{(+)}{R}NH_2{-}OF]\overset{(-)}{F} \longrightarrow RN{=}O + 2HF$$
$$\text{or } [RNH{-}OF] + HF \text{ (with } \uparrow\text{)}\ .$$

One of the intermediate stages in the low-temperature (−78° or −40°C) oxidation of olefins and alkynes by oxygen difluoride probably involves the addition of F–OF to the double or triple bond[32]. Perfluoroethylene, perfluoropropene, perfluorobut-2-ene, and perfluorocyclobutene are less reactive with respect to oxygen difluoride: the reactions of these compounds with OF_2 require thermal or photochemical activation[33]. It is believed that in this case the OF_2 molecule adds to the double bond, but the resulting hypofluorites undergo further reactions, as in the reaction between OF_2 and unsaturated hydrocarbons. When OF_2 reacts with tetramethylallene, the hypofluorite (I) may be formed as an intermediate, which is converted further into compounds (II) and (III):[34]

$$Me_2C{=}C{=}CMe_2 \xrightarrow[-78°]{OF_2} \left[Me_2C{=}\underset{\displaystyle FO\ \ F}{C}{-}CMe_2\right] \rightarrow Me_2\underset{\displaystyle F}{C}{-}\underset{\displaystyle O}{C}{-}\underset{\displaystyle F}{C}Me_2 +$$
$$\text{(I)} \qquad\qquad \text{(II)}$$
$$+\ Me_2\underset{\displaystyle F\ \ O}{C}{-}\underset{\displaystyle O}{C}(Me) = CH_2 + HF\ ,$$
$$\text{(III)} \qquad\qquad (Me{=}CH_3)$$

The thermal (at 50–90°C) or photochemical (λ = 3660 Å; 0°C) reaction of oxygen difluoride with carbonyl sulphide[35], $OF_2 + S = CO \rightarrow F_2SO + CO$, may be regarded as yet another example of the addition of OF_2.

The reaction of oxygen difluoride with carbonyl fluoride in the presence of a catalyst (CsF for RbF) at 25°C gave bis(trifluoromethyl) trioxide[36]: $OF_2 + 2F_2CO = CF_3OOOCF_3$. CF_3OOOCF_3 is formed in low yields when sodium trifluoroacetate is fluorinated[37]. CF_3OOOCF_3 is quite stable at room temperature, decomposing slowly at

70°C with formation of CF_3OOCF_3 and oxygen. The catalytic synthesis of CF_3OOOCF_3 proceeds via several stages[36,38]:

$$(1)\ COF_2 + MF \rightarrow M^+OCF_3^-, \qquad (2)\ OF_2 + CF_3O^- \rightarrow CF_3OOF + F^-,$$
$$(3)\ CF_3OOF + CF_3O^- \rightarrow CF_3OOOCF_3 + F^-, (4)\ CF_3OOF + COF_2 \rightarrow CF_3OOOCF_3.$$

Yet another method for the preparation of bis(trifluoromethyl) trioxide was described recently[39]: it involves the reaction of carbonyl fluoride with di(fluoroxy)difluoromethane in the presence of CsF. Simultaneously with the work of Anderson and Fox[39], a method was described for the preparation of CF_3OOOCF_3 by the reaction of $F_2C(OF)_2$ with caesium trifluoromethoxide in the presence of CsF.[40] In addition to bis(trifluoromethyl) trioxide, CF_3OF, $CF_3OOC(O)F$, and $CF_3OOOCF_2OOCF_3$ are formed by this reaction. The last compound is much less stable than CF_3OOOCF_3 or $CF_3OOOC_2F_5$ and decomposes explosively at 40°C.

The hypothesis postulating oxygen difluoride as a source of OF radicals in reactions involving it appears fairly reasonable. The possibility of the stabilisation of the OF group as a cation must be viewed with restrained optimism: even one of the most probable compounds in which OF^+ might exist, namely $[FO]^+[SbF_6]^-$, could not be obtained by the reaction of OF_2 and SbF_5,[16,41] although the OF_2 molecule, which has the same electronic structure as the OF^+ cation, exists and is quite stable.

In connection with the search for methods of synthesising OF radicals, the behaviour of oxygen difluoride was studied in recent years under conditions leading to its dissociation. The photochemical decomposition of OF_2 in the temperature range 15–45°C has the following mechanism[42]:

$$OF_2 \xrightarrow{h\nu,3650\ Å} F + OF,$$
$$F + F + M = F_2 + M,$$
$$OF = {}^1/_2F_2 + {}^1/_2O_2 .$$

The slow reaction $F + OF_2 = F_2 + OF$, the activation energy of which exceeds 15 kcal mole^{-1},[42] is also possible.

The thermal decomposition of OF_2 into fluorine and oxygen has been investigated[43] in a nickel flow reactor at temperatures in the range 500–700°C. The OF radicals were not detected mass-spectrometrically in the samples removed from the reactor: the ratio of the peak intensities for $m/e = 35$ (OF) and 54 (OF_2) did not differ from the ratio usually observed in the mass spectrum of OF_2. Nor were OF radicals detected in a study of the pyrolysis of OF_2 on heated metallic filaments[44]. The attempt at a mass-spectrometric detection of OF radicals in a stream of oxygen difluoride passed through a microwave discharge also proved unsuccessful[44]. OF radicals were not found to accumulate in an OF_2 specimen subjected to ionising radiation at −196°C.[20]

The mechanism of the decomposition of OF_2 in a shock wave (590–1030°C) and in a static reactor (290–360°C) has been discussed[45,46]. The decomposition of OF_2, which begins after a short induction period, proceeds for a time as a first-order reaction[46], but the overall kinetics of the thermal composition of OF_2 are not consistent with a unimolecular reaction[43,46]. The addition of oxygen does not influence the rate of the thermal decomposition of OF_2 and the addition of fluorine inhibits it. It is suggested[11] that the inhibiting effect of fluorine can be accounted for by the reaction $F_2 + OF = OF_2 + F$. Analysis of the literature data[43,45–47] and the results obtained in a study of the decomposition of OF_2 in a shock wave tube (500–1120°C) enabled Lin and Bauer[11] to suggest a mechanism for the thermal decomposition of OF_2 similar to that for the photochemical decomposition:

$$OF_2 + M \overset{a}{\rightleftarrows} F + OF + M,$$
$$2\,OF \xrightarrow{b} 2F + O_2,$$
$$2F + M \rightleftarrows F_2 + M .$$

Reaction (a) determines the rate of decomposition, its activation energy being 30–40 kcal mole^{-1} according to a number of data[11,43,45–47]. In the temperature range 500–960°C, $k_a = 10^{16\cdot7}\exp(-45\,500/RT)$ cm^3 mole^{-1} s^{-1}.[48] The following mechanism has been postulated for reaction (b):

$$FO + OF \rightarrow (F{-}O{-}O)^* + F + 30\ \text{kcal (fast)},$$
$$(FO_2)^* \rightarrow F + O_2\ \text{(very fast)}.$$

The existence of OF radicals could be demonstrated only with the aid of the matrix isolation technique combined with infrared spectroscopy[49]. The radicals were obtained by the photolysis of OF_2–N_2 or OF_2–Ar mixtures deposited on caesium bromide with the ratio of the number of moles of the matrix to the number of moles of the reactant $M/R = 40$. The absorption band at 1028 cm^{-1} in an argon matrix and a doublet at 1025 and 1030 cm^{-1} in a nitrogen matrix arose after the photolysis of the mixtures deposited at 4°K and disappeared on heating the matrix to 40–45°K. The frequency shift observed in the spectra on photolysis of $^{18}OF_2$ agrees with the calculation on the assumption that the absorption is due to the OF radical. The vibration frequency of the OF radical is 1028 cm^{-1}—the maximum frequency of the OF stretching vibrations in the compounds, including OF_2. Special experiments with the addition of nitrous oxide to the mixture of gases deposited for photolysis revealed the cause of the appearance of a doublet in the nitrogen matrix. The 1025 cm^{-1} band is due to OF radicals in matrix cages containing N_2O and the 1030 cm^{-1} band is due to OF radicals in cages without N_2O. Nitrous oxide is formed as an impurity in the isolating matrix by the reaction of atomic oxygen with N_2 molecules. The low efficiency of the emission at a wavelength of 3650 Å in relation to the generation of OF radicals, compared with gas-phase reactions[26,42], indicates an appreciable role of the cage effect in the matrix photolysis of OF_2.

The yield of OF radicals increases appreciably in the photolysis of OF_2 in a nitrogen matrix in the presence of nitrous oxide or carbon dioxide[50]. One of the pathways for the destruction of radicals is the recombination reaction $F + OF = OF_2$. In the presence of nitrous oxide fluorine atoms are consumed in the reaction

$$F + N_2O \rightarrow OF + N_2 \qquad (**)$$

which constitutes an additional source of OF radicals. According to reaction (**), the lower limit of the bond energy in the OF radical may be estimated as about 40 kcal. An increase of the yield of OF radicals was achieved also in experiments with added CO_2, but the mechanisms of the action of the CO_2 and N_2O additives are different. Fluorine atoms do not react with carbon dioxide under the conditions of matrix photolysis:

$$F + CO_2 \not\rightarrow OF + CO .$$

Probably the following reactions take place in the photolysis of an OF_2–CO_2 mixture:

$$O + CO_2 \rightarrow CO_3,$$
$$F + CO_3 \rightarrow OF + CO_2 .$$

It is also possible that the presence of CO_2 in the matrix and the reaction

$$O + CO_2 \overset{h\nu}{\rightleftarrows} CO_3$$

extend the migration region of O atoms and increase thereby the probability of the reaction $O + F \rightarrow OF$.

The strength of the bonds in the OF radical is sufficiently high for the radicals to exist as stable entities, for example at room temperature. The numerous unsuccessful attempts to detect OF radicals in the gas phase are evidence of their extremely high reactivity. The stabilisation of OF is possible only in an inert matrix over a very narrow temperature range.

2. The Reaction of Fluorine with Oxygen

The term "polyoxygen difluorides" embraces oxygen fluorides the molecules of which contain more than one oxygen atom. Polyoxygen difluorides are very unstable compounds, which decompose considerably below room temperature. They cannot be obtained simply by heating a mixture of fluorine and oxygen. Nevertheless at an elevated temperature fluorine interacts with oxygen and if provision is made for the stabilisation of the reaction products, the fluorine–oxygen compound formed may be isolated. When fluorine and oxygen are passed through a quartz reactor heated to 240–500°C with subsequent quenching of the gases by contact with a surface cooled to −196°C, it is possible to obtain O_2F radicals in an amount sufficient to record their ESR spectrum[51]. In the synthesis of dioxygenyl compounds by heating fluorine, oxygen, and arsenic or antimony pentafluorides to 130–200°C,[41] O_2F radicals are probably formed initially:

$$F_2 \rightleftarrows 2F,\ O_2 + F \rightarrow O_2F,$$

and then react further with the Lewis acid:

$$O_2F + AsF_5\ (SbF_5) = O_2AsF_6\ (O_2SbF_6).$$

The stabilisation of unstable species with the aid of a powerful Lewis acid is a procedure widely employed in inorganic synthesis.

Polyoxygen difluorides are synthesised from the elements in a glow discharge where the reaction of fluorine with oxygen under optimum conditions goes almost to completion. The reaction is carried out in a quartz or pyrex discharge tube, the walls of which are maintained at a low temperature. In experiments at a low current, the electrodes consist of copper or nickel plates inserted into the tube with the aid of Teflon stoppers or in some other way. If the experiments are performed at a discharge current exceeding about 50 mA, the electrode shells are cooled with tap water. A stream of a fluorine–oxygen mixture is passed through the discharge at a reduced pressure. The residual pressure in the apparatus is unimportant when polyoxygen difluorides are obtained in a glow discharge. The pressure is maintained in the range from a few tenths to several mmHg. The Table summarises certain data for the reaction of O_2 and F_2 in a glow discharge. The synthesis of O_2F_2, O_3F_2, and O_4F_2 in an electric discharge from oxygen difluoride and fluorine[52] is analogous to the syntheses of the above compounds from the elements and is of no preparative interest, since oxygen difluoride is less readily available as a starting material than oxygen.

Apart from the flow discharge, the silent and arc discharges are sometimes employed for the synthesis of organic compounds. The reaction of fluorine with oxygen in discharges of this type has not been investigated in sufficient detail. The authors of a study[57] published in 1909 did not obtain oxygen fluoride by passing fluorine and oxygen through an arc discharge and a tap cooled with liquid air. In subsequent years the synthesis of oxygen fluorides in an electric arc was apparently not investigated. The synthesis of O_2F_2 and O_4F_2 in a silent discharge cannot compete as regards the yield of products per unit time and the energy yield with the synthesis of these compounds in a glow discharge and is of interest only within the framework of the study of the mechanism of the reaction of fluorine and oxygen in electric discharges.

Preparation of polyoxygen difluorides.

Reaction equation	Refs	Typical conditions of synthesis			
		compn. of initial mixt. (F_2:O_2 by volume)	flow rate, litre h^{-1}*	Current, mA	Temp. of cooling bath, °C
$O_2 + F_2 = O_2F_2$	53	1:1	~1—~10	~10—~50	−196 or −183
$3O_2 + 2F_2 = 2O_3F_2$	54	2:3	2—2.5	25—30	−196 or −183
$2O_2 + F_2 = O_4F_2$	55	1:2	0.12	4—5	from −213 to −196
$5O_2 + 2F_2 = 2O_5F_2$	56	2:5	0.006—0.008	power ~ 5 W	−213 (−196)
$3O_2 + F_2 = O_6F_2$	56	1:3	0.015—0.022	Power 2-6 W	−213

*Volumes under normal conditions.

Dioxygen difluoride with an admixture of other polyoxygen difluorides was obtained by the action of ionising radiation on a mixture of fluorine and oxygen at −196°C.[58] The apparatus used in this method of synthesis is more complex than the apparatus necessary to synthesise dioxygen difluoride in a discharge. The radiolysis of oxygen difluoride at −196°C leads to the decomposition of OF_2 into the elements with formation of a certain amount of dioxygen difluoride[20].

The available literature data suggest that a gas-phase photochemical reaction can occur between fluorine and oxygen. By keeping a mixture of fluorine, oxygen, and AsF_5 or SnF_5 in the light, the dioxygenyl salts O_2AsF_6 and O_2SbF_6 were obtained[59]. Probably the O_2F radical formed initially reacts with the Lewis acid ($O_2F + EF_5 = O_2EF_6$) as in the thermal reaction[41]. When a mixture of fluorine and oxygen was irradiated by light from a mercury lamp, the formation of dioxygen difluoride was noted[60]. Bearing in mind that appreciable decomposition of O_2F_2 begins at a temperature as low as −100°C,[61] it is very remarkable that the experiments of Levy and Copeland were carried out at −42°C.

As a result of the irradiation of a mixture of fluorine and ozone with ultraviolet light in a reaction vessel thermostatted at −153°C,[62] O_2F_2 and OF_2 were formed. It is suggested that the reaction proceeds as follows:

$$F_2 \xrightarrow{h\nu,3650\text{Å}} 2F,\ F + O_3 \rightarrow O_2 + OF,$$

$$OF + OF = O_2F_2,\ OF + F = OF_2,\ OF + F_2 = OF_2 + F.$$

In analogous experiments at −78°C only oxygen difluoride was obtained[62]. If the photochemical reaction of fluorine with oxygen is carried out at a still higher temperature (0°C and 20°C), the decomposition of ozone without the formation of oxygen fluorides is observed[63]:

$$F_2 + O_3 \xrightarrow{h\nu,3650\text{Å}} F_2 + {}^3/_2O_2.$$

Among all the reactions enumerated and leading to the formation of dioxygen difluoride and other polyoxygen

difluorides, only the reaction of fluorine with oxygen in a glow discharge can be regarded as a simple and readily available method of synthesis of polyoxygen difluorides.

The most probable mechanism of the synthesis of polyoxygen difluorides from the elements includes as the primary step the reaction of atomic fluorine with molecular oxygen:

$$F + O_2 = O_2F$$

and further stages involving O_2F radicals, for example:

$$O_2F + F = O_2F_2,$$
$$O_2F + O_2F = O_4F_2,$$
$$O_2F + O_2 \rightarrow O_4F \xrightarrow{+O_2F} O_6F_2 .$$

In this mechanism the dissociation of O_2 molecules is not regarded as an essential stage of the synthesis. Possibly, in general any activation of oxygen is superfluous. Irradiation of F_2–O_2 mixtures under matrix conditions at 4° or 20°K by ultraviolet light, which dissociates only fluorine molecules, leads to the formation of O_2F radicals[64,65]. Atomic oxygen is probably formed when F_2–O_2 mixtures are passed through a glow discharge, but in this case too there is no need to include in the mechanism for the synthesis of polyoxygen difluorides reactions involving atomic oxygen. An equimolar fluorine–oxygen mixture is almost completely converted into O_2F_2 with a low energy expenditure per unit volume of the reacting gases with a negligibly low degree of dissociation of oxygen[66]. With increase of energy expenditure, the dissociation of O_2 molecules becomes more pronounced and the synthesis of O_2F_2 is accompanied by the formation of ozone as a side reaction.

The preparation of unstable polyoxygen difluorides has been fairly thoroughly investigated, but a method for the synthesis of the thermally stable oxygen difluoride from the elements is unknown. The formation of trace amounts of OF_2 in the synthesis of O_2F_2 has been noted[44] but the possibility of obtaining OF_2 in an appreciable yield in a glow discharge is doubtful. The formation of O_2F_2 or another polyoxygen difluoride, which does not require the dissociation of O_2 molecules, has a clear advantage over the synthesis of OF_2. Under the conditions where the degree of dissociation of O_2 becomes appreciable, the formation of OF_2 may be hindered by the consumption of O atoms in the synthesis and decomposition of oxone: $O + O_2 = O_3$ and $O_3 + O = 2O_2$. One must also assume the possibility of the recombination of OF radicals with formation of O_2F_2:

$$OF + OF = O_2F_2 (S),$$

where (S) is a cold wall. Finally it is extremely likely that the absence of OF_2 from the product of the reaction of fluorine with oxygen in a glow discharge is simply due to the high vapour pressure of OF_2, which is about 1 mmHg at −196°C. It is difficult to freeze a substance with such a vapour pressure on the cold wall of the discharge tube and thereby prevent its decomposition in the hot reaction zone.

3. Dioxygen Difluoride

In order to prepare dioxygen difluoride, an equimolar mixture of fluorine and oxygen or one containing a slight excess of fluorine is passed through a glow discharge[53,67,68]. Dilution of the initial equimolar mixture with argon hardly alters the degree of its conversion into dioxygen difluoride[66]. When fluorine, oxygen, and nitrogen are passed through a glow discharge in a low-temperature reactor, dioxygen difluoride is also formed but in this case a certain amount of oxygen also enters into the reaction as a result of which trifluoroamine oxide is formed[69].

The dioxygen difluoride obtained in the glow discharge is sometimes contaminated by one or several substances, for example SiF_4 and O_4F_2. The decomposition of the less stable oxygen fluorides present in the freshly prepared O_2F_2 specimen can probably account for the increase of pressure in a closed system observed when O_2F_2 is heated to a temperature close to −160°C. Usually the impurity content is small and does not affect appreciably the results of the chemical analysis of O_2F_2 and does not prevent its further employment. Brief heating above −78°C causes partial decomposition of O_2F_2 and therefore O_2F_2 can be distilled from one compartment of a closed system to another, without removing by the vacuum pump a "cushion" of fluorine and oxygen, only with the aid of liquid helium.

Dioxygen difluoride melts at −163.5°C [53] (−154°C according to later data[70]) and decomposes below the boiling point; the normal boiling point found by extrapolating the the temperature variation of the vapour pressure is −57°C.[61] Solid O_2F_2 is orange-yellow in colour (yellow according to some observations[58,70]), turning into an oily bright-red liquid on fusion. With increase of temperature, the molar extinction coefficient of O_2F_2 rises[71]. The density of O_2F_2 decreases from 1.912 g cm^{-3} at −165°C to about 1.44 g cm^{-3} at −57°C.[61] The vapour pressure of O_2F_2 in the temperature range between −132° and −100°C is described by the equation[61] $\lg p$ (mmHg) = 7.515 − 1000/T, the decomposition of O_2F_2 beginning above −100°C. The vapour pressure of O_2F_2 is (in mmHg) 0.01 at −168°C,[1] 0.05 at −163°C,[72] 1 at −143°C,[72] 3 at −132°C,[61] and 257 at −79.5°C.[61] $\Delta H^\circ_{f298}[O_2F_2(\text{gas})]$ found in a study of the decomposition of dioxygen difluoride is 4.73 kcal mole^{-1}.[73]

It has been established by microwave spectroscopy[74] that the O_2F_2 molecule consists of an F–O–O–F atomic chain bent in space and characterised by the following parameters: r(O–O) = 1.217 Å, r(O–F) = 1.575 Å, ∠ OOF = 109°30′, a dihedral angle of 87°30′, and a dipole moment of 1.44 D. Quantum-mechanical calculation shows[75] that the configuration of the O_2F_2 molecule with a dihedral angle of 85°C is separated from the *cis*- and *trans*-configurations by energy barriers of 16.62 and 20.83 kcal mole^{-1} respectively. The spectrum of $^{16}O_2F_2$ recorded at −196°C contains absorption bands at 1306 cm^{-1} (O–O stretching vibration), 621 cm^{-1} (O–F symmetrical stretching vibration), 615 cm^{-1} (O–F antisymmetric stretching vibration), 457 cm^{-1} (O–O–F antisymmetric deformation vibration), 369 cm^{-1} (O–O–F symmetrical deformation vibration), and 205 cm^{-1} (torsional vibration)[70,76]†.

The dioxygen difluoride molecule is diamagnetic. Pure O_2F_2 molecules do not give rise to an ESR signal[58]. The paramagnetic centres in dioxygen difluoride are the O_2F radicals[77,78] the presence of which can be accounted for by the partial decomposition of the compound.

An unusually low ^{19}F chemical shift (−865 p.p.m.) has been found[79] in O_2F_2 (10% solution of O_2F_2 in CF_3Cl), which is evidence of very weak screening of the fluorine nuclei. Subsequent studies[80–82] confirmed this report[79]. δ = −865 p.p.m. was found for liquid O_2F_2 at −128°C using $CFCl_3$ as an external standard[81]. Extrapolation to

† After this paper had been sent to the Editors, D. J. Gardiner, N. J. Lawrence, and J. J. Turner published the results of a study of the vibrational spectra of O_2F_2 [J. Chem. Soc., A, 400 (1971)].

infinite dilution of O_2F_2 in CF_3Cl at −83°C gave δ = −825 p.p.m.[82] The ^{17}O shift in the $^{17}O_2F_2$ molecule is[80,83] −647 p.p.m. relative to $H_2{}^{17}O$.

The O–O distance in the O_2F_2 molecule is close to the interatomic distance in the oxygen molecule (1.207 Å), r(O–F) in O_2F_2 considerably exceeds r(O–F) in the OF_2 molecule (1.39–1.41 Å). With these interatomic distances, there should be a strong O–O bond and a weak O–F bond in O_2F_2. The following dissociation energies have been found mass spectrometrically[72]: $D(FO-OF) = 103.5 \pm 5$ kcal mole^{-1} and $D(F-O_2F) \simeq D(O_2-F) \simeq 18$ kcal mole^{-1}. The fluorine atoms weakly bound to oxygen are readily split off as a result of which O_2F_2 is extremely reactive even at a low temperature.

The kinetics of the thermal decomposition of dioxygen difluoride have been investigated as early as the 1930's.[67,84,85] In the temperature range between −60° and −25°C the decomposition reaction is homogeneous and unimolecular with an activation energy of about 17 kcal mole^{-1}. As was to be expected, the activation energy for the decomposition is almost identical with the O–F bond dissociation energy. Addition of fluorine activates the decomposition of O_2F_2.[85] The most probable decomposition mechanism[11] involves O_2F radicals:

$$O_2F_2 + M \rightarrow F + O_2F + M,$$
$$O_2F + M \rightarrow F + O_2 + M,$$
$$F + O_2F_2 \rightarrow F_2 + O_2F,$$
$$F + F + M \rightarrow F_2 + M\ .$$

The decomposition mechanism[86] the initial stage of which is the formation of OF radicals,

$$O_2F_2 \rightarrow OF + OF\ ,$$

is unlikely, since it requires a considerable activation energy[11]. The method of chemical analysis of dioxygen difluoride is based on the determination of the amount of fluorine and oxygen obtained after the decomposition of O_2F_2.

The O_2F radical, detected by infrared spectroscopy in the photolysis of OF_2–O_2 or F_2–O_2 mixtures under matrix isolation conditions[64,65,87], plays an important role in the chemistry of low-temperature oxygen fluorides. It has also been noted[64] that O_2F radicals are generated when oxygen difluoride is exposed to an ultrahigh frequency glow discharge. When the matrix isolating the radicals (oxygen, nitrogen, or argon) becomes softened, recombination takes place[64]:

$$O_2F + F = O_2F_2,$$
$$O_2F + O_2F = O_4F_2\ .$$

The dioxygen monofluoride radical consists of the atomic chain O–O–F. Quantum-mechanical calculation[88] shows that the asymmetric OOF structure is energetically more favourable to the extent of almost 100 kcal mole^{-1} compared with the symmetrical structure OFO. The vibration frequencies in the infrared spectrum of $^{16}O_2F$ are[87] 1495 (ν_1), 585 (ν_2), and 376 cm^{-1} (ν_3). The force constant k_{O-O} for O_2F is close to the value in the oxygen molecule and lies in the range 8–12 mdyn Å^{-1} characteristic of double bonds:

	k_{O-O}, mdyn Å^{-1}		
O_2F	10.45[64]	10.47[65]	10.50[87]
O_2	11.43[89]		

The dissociation energy of the O–O bond in O_2F is 110 kcal according to mass-spectrometric data[72,90], i.e. the addition of the F atom to the O_2 molecule does not result in an appreciable loss of strength by the O–O bond. The average lifetime of dioxygen monofluoride depends on the surrounding medium and at temperatures between −180° and −160°C amounts to minutes[91]. Generally speaking the dioxygen monofluoride radical resembles stable molecular radicals more than unstable radicals such as OF. If the interpretation[92] of the results obtained in the study of the decomposition of O_2BF_4 is correct, the radicals O_2F may exist for a long time in the gas phase at room temperature. In this connection, it is interesting to note that NF_2, an electronic (but not structural) analogue of O_2F, is stable at temperatures considerably exceeding room temperature, while the radical OOCl, which has the same structure, is unstable in the gas phase.

Exhaustive compilations of the reactions of O_2F_2 investigated up to 1963 have been published[1,93]. This review presents certain data taken from Streng[1,93] and also from later sources.

Dioxygen difluoride does not react with Pyrex glass and quartz. In the recording of the infrared spectrum of O_2F_2, silver chloride and high-pressure polyethylene were employed[70]. Polytetrafluoroethylene apparently reacts with O_2F_2.[74] In contact with platinum, O_2F_2 explodes[1]. The effect of atomic hydrogen at −196°C leads to the substitution of F by H atoms and to the dissociation of the O–O bond in dioxygen difluoride[93]:

$$2\,O_2F_2 + 10\,H = 4\,HF + H_2O_2 + 2\,H_2O\ .$$

At −140°C O_2F_2 does not react with N_2O, oxidises NO to NO_2 and FNO_3 at temperatures between −160°C and −70°C, and forms with nitrogen dioxide an unidentified unstable white solid compound[16]. It converts N_2F_4 into NF_3 at −100°C but at −150°C it does not react with N_2F_4 and N_2F_2.[1] The reaction of O_2F_2 with phosphorus trifluoride[93] at −148°C yields phosphorus pentafluoride and a substance to which the formula $(POF_3)_n$ was attributed. It is quite possible that the postulated polymer $(POF_3)_n$ contained dioxygenyl hexafluorophosphate. Sulphur tetrafluoride reacts vigorously with O_2F_2 at about −140°C:

$$SF_4 + O_2F_2 \rightarrow SF_6 + O_2\ .$$

In the presence of perchloryl fluoride as a solvent, it is possible to obtain an extremely unstable product of the addition of O_2F_2 to sulphur tetrafluoride[93]:

$$O_2F_2 + SF_4 \rightarrow O_2SF_6\ .$$

The reactions of O_2F_2 with chlorine and bromine fluorides have been investigated in detail. In the temperature range between −154°C and −143°C, chlorine monofluoride forms with O_2F_2 a violet compound $(O_2ClF_3)_n$:[93,94]

$$n O_2F_2 + n\,ClF \rightarrow (O_2ClF_3)_n\ .$$

Chlorine dioxide trifluoride can be stored for a long time at −78°C. This compound does not contain ions and does not dissociate in hydrogen fluoride solution[95]. Other pathways for the formation of chlorine dioxide trifluoride involve the reaction of O_2F_2 with HCl:[93,95]

$$O_2F_2 + 2\,HCl \rightarrow 2\,HF + O_2 + Cl_2,$$
$$O_2F_2 + Cl_2 \rightarrow 2\,ClF + O_2,$$
$$O_2F_2 + ClF \rightarrow O_2ClF_3,$$

or the photochemical reaction of ClF_3 with oxygen at −78°C:[95,96]

$$ClF_3 + O_2 \xrightarrow{h\nu,\,2537\,Å} O_2ClF_3\ .$$

The unstable compound O_2BrF_5, which decomposes completely into O_2 and BrF_5 at −100°C, was obtained by the reaction of O_2F_2 with bromine trifluoride[93,97]. At about −140°C hydrogen bromide reacts with an excess of O_2F_2:

$$3\,O_2F_2 + HBr \rightarrow O_2BrF_5 + HF + 2O_2 .$$

At low temperatures iodine pentafluoride does not react with O_2F_2 but at elevated temperatures it is converted into the heptafluoride[93].

XeF_2 has been obtained by the reaction of dioxygen difluoride with xenon at −118°C,[98,99] while elemental fluorine does not react with xenon at room temperatures and above. Some of the reactions of dioxygen difluoride enumerated above constitute the usual type of fluorination; the addition of O_2F_2 molecules to another reactant takes place in the reaction with ClF, BrF_3, or SF_4. The possibility of reactions involving O_2F radicals under mild conditions, where a rapid and uncontrollable decomposition of radicals such as O_2F as well as dioxygen difluoride itself is ruled out, is of considerable interest for preparative inorganic chemistry. The transfer of O_2F radicals is also implied in the reactions of O_2F_2 with Lewis acids—fluoride ion acceptors. Such reactions result in the formation of the O_2^+ cation, which, when combined with the anion of a complex fluorine acid, forms a dioxygenyl salt.

At −183° or −160°C dioxygen difluoride fluorinates sulphur dioxide:

$$SO_2 + O_2F_2 \rightarrow F_2SO_2 + O_2 .$$

Apart from the main product (sulphuryl fluoride), smaller amounts of FSO_2OSO_2F and fluoroperoxysulphuryl fluoride FSO_2OOF are also formed[100,101]. Experiments with the oxygen-17 isotope and by the ^{17}O NMR method showed that the synthesis of FSO_2OOF constitutes a reaction of O_2F_2 with transfer of an O_2F radical. Another example of the transfer of O_2F is the reaction of O_2F_2 with hexafluoropropene[102], which takes place smoothly at −183°C in chlorotrifluoromethane. The reaction results in the formation of a high yield of a mixture of isomers: $CF_3CF(OOF)CF_3$ and $CF_3CF_2CF_2OOF$.

4. Other Oxygen Fluorides: O_3F_2, O_4F_2, O_5F_2, and O_6F_2

a. Trioxygen difluoride. The report[103] of the synthesis of O_3F_2 when a liquid mixture of F_2 and O_2 is irradiated with ultraviolet light was treated sceptically and the possibility of the existence of trioxygen difluoride was not taken seriously until the publication in 1959 of the work of Kirshenbaum and Grosse[54]. The name "ozone fluoride"[54] proposed for O_3F_2 did not become established. Trioxygen difluoride melts at about −189°C and can be supercooled to −196°C. On heating to room temperature, O_3F_2 decomposes completely to fluorine and oxygen, probably with formation of dioxygen difluoride as an intermediate in the thermal decomposition. The activation energy for the decomposition of O_3F_2 in the temperature range between −196° and −157°C was found to be 3.7 kcal mole^{-1}.[54]

The conditions for the synthesis of O_3F_2 and O_2F_2 in an electric discharge differ only by the composition of the initial gas mixture: the $F_2 : O_2$ ratio is 2 : 3 for O_3F_2 compared with 1 : 1 for O_2F_2. According to Kirshenbaum and Grosse[54], a mixture of two volumes of fluorine and three volumes of oxygen is quantitatively converted into O_3F_2 in a glow discharge, the yield reaching 3–4 g h^{-1}. We may note that the desired product can be by no means always synthesised. As a rule, O_2F_2 is formed in the synthesis of O_3F_2 and the oxygen present in excess of the amount required for the synthesis of O_2F_2 either does not react at all or is converted into ozone.

The ESR spectra of O_2F_2 and O_3F_2 have been found to be identical[77]. The paramagnetic centres in both fluorides are the O_2F radicals. The concentration of free radicals in O_3F_2 specimens is higher by two powers of ten than in dioxygen difluoride specimens and reaches 5–10 mole %. It is believed[77] that such a high concentration of O_2F is caused by the thermal decomposition of O_3F_2.

Investigation of the properties of O_3F_2 by spectroscopic methods gave rise to doubts concerning the individuality of trioxygen difluoride. Different models have been proposed[44,80,81,83] whereby it might be possible to account for the characteristics of the ^{19}F and ^{17}O NMR spectra and the mass spectrum of O_3F_2. Probably it is most correct to regard trioxygen difluoride as a mixture of dioxygen difluoride and tetraoxygen difluoride in equilibrium with O_2F radicals; this has been demonstrated by Solomon and coworkers[80,83].

O_2F_2 has been obtained by the reaction of fluorine activated in a discharge (atomic fluorine) with O_3F_2 at −196°C, i.e. F atoms add to the O_2F radicals present in trioxygen difluoride. O_3F_2 does not react with molecular fluorine at −196°C.[54] The reaction of O_3F_2 with boron trifluoride yields O_2BF_4 with evolution of fluorine[83]. The stoichiometry of the reaction

$$4\,O_3F_2 + 6\,BF_3 = 6O_2BF_4 + F_2$$

is consistent with the hypothesis that trioxygen difluoride is a mixture of O_2F_2 and O_4F_2.

b. Tetraoxygen difluoride. O_4F_2 has been obtained in a gas discharge reaction of fluorine and oxygen under mild conditions[55,104]. This compound is probably formed as a result of the recombination of O_2F radicals:

$$FO_2 + O_2F = O_4F_2 ,$$

but other reactions cannot be ruled out[58,64]:

$$O_2F + O_2 \rightarrow O_4F \xrightarrow{+F} O_4F_2,$$
$$F + O_4 \rightarrow O_4F \xrightarrow{+F} O_4F_2 .$$

The O_4F_2 molecule probably consists of the atomic chain F–O–O–O–O–F, where the O–O bonds adjoining the fluorine atoms are equivalent and close in strength to double bonds[64]. The dissociation energy of the central O–O bond hardly exceeds about 3 kcal mole^{-1}.[58] The ESR spectrum of O_4F_2 is determined[105], as for O_2F_2 and O_3F_2, by O_2F radicals. The red-brown solid O_4F_2 melts at −191° ± 2°C and explodes on being heated rapidly. The O_4F_2 vapour pressure is 0.25 mmHg at −183°C.[104] The half life of O_4F_2 at −183°C is 16 days but at −196°C the compound or its solutions in carbon tetrafluoride can be stored for several weeks[104]. The final products of the thermal decomposition of O_4F_2 are fluorine and oxygen. Like O_2F_2, tetraoxygen difluoride forms a dioxygenyl salt with boron trifluoride[83,92]. At −196°C O_4F_2 reacts with tetrafluorohydrazine, forming nitrogen trifluoride[104].

c. Higher representatives of the polyoxygendifluoride family. In 1966 the preparation of oxygen fluorides with the empirical formulae O_5F_2 and O_6F_2 was described[56]. The first compound decomposes slowly at −196°C and rapidly at −183°C, the final decomposition products of O_5F_2 being fluorine and oxygen. The second compound decomposes slowly on heating from −213° to −183°C with evolution of ozone, while rapid heating from −183°C results in an explosion of O_6F_2.

The solubility of O_5F_2 and O_6F_2 in liquid oxygen difluoride is about 5 wt.% at −208° and −213°C respectively. The structures of O_5F_2 and O_6F_2 are unknown. The attempts to obtain fluorides with a higher oxygen content from an initial $5O_2-F_2$ mixture by the method described for the synthesis of O_5F_2 and O_6F_2 were unsuccessful[56]. The preparation of a mixture of oxygen fluorides, one of the components of which might have been O_6F_2, was reported in 1969.[58]

The thermal stability of polyoxygen difluorides decreases with increasing number of oxygen atoms in the O_nF_2 molecule: for $n > 2$, the compounds are extremely unstable or their very existence is debatable. However, CF_3OOF, CF_3OOCF_3, and CF_3OOOCF_3 (and possibly $CF_3OOOOCF_3$), i.e. perfluoroalkyl derivatives of polyoxygen difluorides, exist and are much more stable than the corresponding oxygen fluorides[2]. The increase of the stability of the chain of oxygen atoms is an extremely interesting result of the substitution of fluorine atoms by perfluoroalkyl radicals and merits a more detailed investigation.

III. DIOXYGENYL COMPOUNDS

The existing methods for the synthesis of dioxygenyl compounds consist in the oxidation of molecular oxygen:

$$O_2 + PtF_6 \rightarrow O_2^+PtF_6^-$$

and the reaction of oxygen fluorides (O_2F radicals) with the corresponding Lewis acids:

$$O_2F + BF_3 \rightarrow O_2F \cdot BF_3 \rightarrow O_2^+BF_4^-$$

or

$$O_2F + EF_5 \rightarrow O_2F \cdot EF_5 \rightarrow O_2^+EF_6^- \ (E=P, As, Sb, Bi)$$

1. Dioxygenyl Hexafluoroplatinate

Dioxygenyl hexafluoroplatinate was described in 1962.[4,106] It is formed in the fluorination of platinum or its salts in glass and quartz vessels. The oxygen required for the synthesis of O_2PtF_6 is evolved in this case when fluorine acts on the walls of the reaction vessel. Treatment of platinum sponge with a mixture of fluorine and oxygen at 450°C or heating of platinum sponge in an atmosphere of OF_2 also leads to the synthesis of O_2PtF_6. At room temperature O_2PtF_6 was obtained by tensimetric titration of oxygen with platinum hexafluoride.

The crystal lattice energy of $O_2^+PtF_6^-$ calculated from the Kapustinskii equation is −125 kcal mole^{-1} and the electron affinity of platinum hexafluoride has been estimated as not less than 7 eV. Platinum hexafluoride is a powerful oxidising agent capable of forming crystalline compounds on reaction with molecular oxygen or xenon. However, the attempts to carry out the reaction between PtF_6 and krypton, nitrogen, or nitrogen trifluoride were unsuccessful[107,108].

Dioxygenyl hexafluoroplatinate is a red solid which sublimes above 90°C in a vacuum and melts with decomposition at 219°C.[106] Two modifications of O_2PtF_6 have been established by X-ray diffraction: a rhombohedral low-temperature modification and a high-temperature cubic modification with a unit cell parameter $a = 10.032$ Å and $z = 8$. The $r(O-O) = 1.13$ Å distance obtained in an X-ray diffraction study[106] is not entirely reliable owing to the difficulty of determining the positions of the light O atoms in the presence of the heavy Pt atoms. In a neutron diffraction study[109] of O_2PtF_6 powder, only the limits of $r(O-O)$ were found: 0.9–1.4 Å. The magnetic susceptibility of this compound in the range 88–294°K obeys the Curie–Weiss law. The magnetic moment $\mu_{eff} = 2.57$ Bohr magnetons[106] is close to the pure spin moment for two unpaired electrons (2.83 Bohr magnetons); one unpaired electron belongs to the O_2^+ and the other to the octahedral PtF_6^- ion. The magnetic moment $\mu_{eff}(O_2^+) = 1.57$ Bohr magnetons at room temperature[110]. In the Raman spectrum of O_2PtF_6 the O_2^+ vibration frequency is 1837 cm^{-1}.[108]

Dioxygenyl hexafluoroplatinate reacts vigorously with water, evolving oxygen and a small amount of ozone. The solution formed on hydrolysis contains PtF_6^{2-} ions and the residue consists of hydrated PtO_2. The hydrolysis of O_2PtF_6 by water vapour takes place similarly[4]. The reaction of O_2PtF_6 vapour with heated potassium fluoride or the reaction of potassium fluoride with O_2PtF_6 in iodine pentafluoride leads to the substitution of the O_2^+ cation by K^+. The reactions of O_2PtF_6 with bromine trifluoride and selenium tetrafluoride proceed as follows:

$$O_2PtF_6 + 3BrF_3 \rightarrow (BrF_3)_2PtF_4 + BrF_5 + O_2,$$
$$O_2PtF_6 + 3SeF_4 \rightarrow (SeF_4)_2PtF_4 + SeF_6 + O_2.$$

The reactions of O_2PtF_6 with ClF_3 and IF_5 yielded difluorochlorinium and tetrafluoroiodinium hexafluoroplatinates[4,106]. Dioxygenyl hexafluoroplatinate reacts vigorously with benzene, cyclohexane, and pyridine but not with carbon tetrachloride.

2. Dioxygenyl Compounds of Group V Elements

The synthesis of salts with the general formula O_2EF_6 (E = P, As, or Sb) was reported in 1964.[111,112] In addition a patent[113] taken out by Young et al.[111] reports the bismuth compound O_2BiF_6. The method of synthesis of the compound O_2EF_6 is based on the reaction of dioxygen difluoride with fluorine-containing Lewis acids—the pentafluorides of Group V elements. The synthesis is carried out at a low temperature by bringing dioxygen difluoride and the condensed pentafluoride into contact, either directly in a discharge reactor where O_2F_2 is obtained or O_2F_2 is distilled into a separate trap containing the other reactant. The end of reaction is indicated by the disappearance of the orange colour of dioxygen difluoride. The solid reaction products are kept for several hours in a vacuum to remove the excess pentafluoride. The dioxygenyl salts of arsenic and antimony are also obtained when daylight is allowed to act on a mixture of oxygen, fluorine, and arsenic or antimony pentafluoride[59]. A thermal synthesis of dioxygenyl compounds was described in 1969.[41] When mixtures of OF_2 and AsF_5 are heated to 200°C and a pressure of 200 atm, dioxygenyl hexafluoroarsenate is formed in a yield up to 80%: $4OF_2 + 2AsF_5 = 2O_2AsF_6 + 3F_2$. A mixture of fluorine and oxygen may be used instead of oxygen difluoride. O_2AsF_6 has been obtained in almost quantitative yield by heating the starting materials in the proportions $F_2 : O_2 : AsF_5 = 1 : 2 : 2$ at 130°C or 200°C and 150 atm for 5–7 days. Similar results were achieved in experiments using antimony pentafluoride as the Lewis acid. The attempts to obtain dioxygenyl salts by this method from BF_3, PF_5, SiF_4, BrF_3, BrF_5, and IF_5 were unsuccessful[41].

a. Dioxygenyl hexafluorophosphate. When O_2PF_6 is prepared by the reaction

$$O_2F_2 + PF_5 \xrightarrow{-126 \text{ or } -100^\circ} O_2PF_6 + {}^1/_2F_2,$$

a certain amount of POF_3 is formed. The solid white dioxygenyl hexafluorophosphate is a very unstable compound which decomposes slowly at −80°C.[111-113]. At room temperature O_2PF_6 decomposes rapidly:

$$O_2PF_6 \rightarrow O_2 + {}^1/_2F_2 + PF_5.$$

Owing to its low thermal stability, O_2PF_6 is not formed when fluorine, oxygen, and PF_5 are heated together[41].

The reaction of O_2PF_6 with water leads to the evolution of oxygen; O_2PF_6 reacts with nitrogen dioxide according to the equation[111]

$$O_2PF_6 + NO_2 = O_2 + NO_2PF_6.$$

b. Dioxygenyl hexafluoroarsenate. Apart from the methods for the preparation of O_2PF_6 enumerated above, the reaction of fluorodiazonium hexafluoroarsenate with oxygen has been mentioned[16]:

$$N_2FAsF_6 + O_2 \xrightarrow{2 \text{ atm}} O_2AsF_6 + N_2 + {}^1/_2F_2.$$

Dioxygenyl hexafluoroarsenate is stable below 100°C but decomposes rapidly at 130–180°C:[111]

$$O_2AsF_6 = O_2 + {}^1/_2F_2 + AsF_5.$$

The O_2^+ peak has been recorded in the mass spectrum of the vapour over a specimen of pure O_2AsF_6 at a pressure of the order of 10^{-6} mmHg and room temperature[111]. X-Ray powder diffraction patterns of O_2AsF_6 and $NOAsF_6$ show that these compounds are isomorphous, which confirms the ionic structure $O_2^+AsF_6^-$. The unit cell parameter of the cubic O_2AsF_6 lattice is $a = 8.00$ Å [111] or 8.10 Å.[59] The infrared spectrum of dioxygenyl hexafluoroarsenate contains a single absorption band at 705 cm^{-1}, which is characteristic of the AsF_6^- ion[41,59,111]. The vibrations of the octahedral AsF_6^- ion at 688, 574, and 375 cm^{-1} and the vibration of the O_2^+ ion at 1858 cm^{-1} are active in the Raman spectrum[114] of O_2AsF_6. A singlet line with a g-factor of 1.9980 has been observed in the ESR spectrum of dioxygenyl hexafluoroarsenate.

The hydrolysis of O_2AsF_6 is described by the equation

$$2\,O_2AsF_6 + H_2O = O_2 + O_3 + HAsF_6,$$

and its reaction with nitrogen dioxide yields a nitronium salt[111].

b. Dioxygenyl fluoroantimonates. In general the reaction between dioxygen difluoride and SbF_5 cannot be described by the equation $O_2F_2 + EF_5 = O_2EF_6 + \frac{1}{2}F_2$ (E = Sb), which is valid for phosphorus and antimony pentafluorides. In contrast to arsenic pentafluoride, SbF_5 is considerably associated and contains fluorine bridge bonds. The existence of polymeric (dimeric and trimeric) fluoroantimonate anions is well known, for example in the compounds $N_2F_3^+Sb_2F_{11}^-$ [115] and $ClO_2^+Sb_3F_{16}^-$ [116] (incidentally, arsenic pentafluoride also forms the dimeric ions $As_2F_{11}^-$)[117]. SbF_5 probably reacts in the monomeric form at an elevated temperature[41]. The composition of the product of the low-temperature reaction of dioxygen difluoride and antimony pentafluoride corresponds more closely to the compound $O_2Sb_2F_{11}$ than to O_2SbF_6.[118] The authors of an early investigation[111] probably synthesised $O_2Sb_2F_{11}$ from dioxygen difluoride and antimony pentafluoride. Little is known about the interaction of antimony trifluoride with dioxygen difluoride; it has only been reported that O_2SbF_6 could not be obtained by the reaction of SbF_3 with O_2F_2.[16]

The face-centred cubic unit cell of O_2SbF_6 is a = 10.13 Å [41] or a = 10.30 Å.[59] Nikitina and Rosolovskii[118] found a = 5.07 Å (z = 1) for the cubic O_2SbF_6 lattice. The compound $O_2Sb_2F_{11}$ is usually amorphous to X-rays; certain specimens give rise to an X-ray diffraction pattern with two intense lines (d = 3.95 and 3.59 Å), the number of lines increasing after fusion of the salt[118]. The infrared spectrum of O_2SbF_6 contains the ~669 cm^{-1} band of the SbF_6^- anion[41,118]. The fluoroantimonate $O_2Sb_2F_{11}$ absorbs at 492 and 665–715 cm^{-1}; it is suggested that the absorption at 492 cm^{-1} is caused by the vibrations of the Sb–F–Sb bridge bond[118]. The O_2^+ vibration is observed in the Raman spectrum of solid O_2SbF_6 at 1862 cm^{-1} or at 1860 cm^{-1} for an O_2SbF_6 solution in SbF_5.[114] The magnetic susceptibility of O_2SbF_6 has been measured in the range 80–333°K.[119] The effective magnetic moment at room temperature is 1.65 Bohr magnetons.

Dioxygenyl fluoroantimonates have been investigated by differential thermal analysis[118]. The endothermic effect in the thermogram of $O_2Sb_2F_{11}$ at 180–185°C corresponds to its fusion, rapid decomposition beginning above 260°C. The thermogram of O_2SbF_6 shows three endothermic effects: at 160–165°C (polymorphic transformation), 240–245°C (decomposition), and about 280°C. The two-stage decomposition process of O_2SbF_6 involves the mechanism

$$2\,O_2SbF_6 \xrightarrow{\sim 240^\circ} O_2 + {}^1/_2F_2 + O_2Sb_2F_{11},$$

$$O_2Sb_2F_{11} \xrightarrow{\sim 280^\circ} O_2 + {}^1/_2F_2 + 2SbF_5.$$

Thus dioxygenyl fluoroantimonates are much more stable to heat than dioxygenyl fluorophosphate and fluoroarsenate. On heating in a vacuum above 130°C, $O_2Sb_2F_{11}$ is converted into O_2SbF_6:

$$O_2Sb_2F_{11} \rightarrow O_2SbF_6 + SbF_5.$$

By heating a mixture of $O_2Sb_2F_6$ and antimony pentafluoride at 180–200°C, it is possible to obtain $O_2Sb_2F_{11}$, i.e. we have the equilibrium

$$O_2Sb_2F_{11} \rightleftharpoons O_2SbF_6 + SbF_5.$$

which is almost completely displaced to the left at room temperature[118].

3. Dioxygenyl Tetrafluoroborate

Dioxygenyl tetrafluoroborate was apparently obtained in 1960 from boron trifluoride, oxygen, and fluorine in a glow discharge[16]. In 1964 the synthesis of O_2BF_4 by the reaction of dioxygen difluoride with boron trifluoride at −126°C was reported[112]. Subsequently[83,92] the reaction of O_4F_2 with BF_3 was investigated: $\frac{1}{2}O_4F_2 + BF_3 = O_2BF_4$. It was established[92] that at −138°C O_4F_2 reacts with BF_3 much more vigorously than does O_2F_2 at −126°C. The difference between the reaction rates can be readily accounted for: O_4F_2 apparently dissociates more readily into O_2F radicals than does O_2F_2, but this difference is not fundamental since it has been shown[58] that the reaction of several millimoles of BF_3 with dioxygen difluoride at −126°C terminates in 10 min, which is comparable to the rate of reaction between O_4F_2 and BF_3.[92] It is known[58] that O_2BF_4 is formed when bremsstrahlung with an energy of 3 MeV acts upon a mixture of BF_3, O_2, and F_2 in a sapphire reactor.

X-Ray powder diffraction patterns of O_2BF_4 and $NOBF_4$ show that these compounds are isomorphous. The orthorhombic unit cell of O_2BF_4 has the parameters a = 8.77 Å, b = 5.58 Å, and c = 7.05 Å.[58] The effective

magnetic moment of O_2BF_4 is 1.7 Bohr magnetons[120]. The unpaired electron of the cation has been detected by ESR spectroscopy[58,112]. The vibrations of the BF_4^- ion have been found in the infrared spectrum[121] of O_2BF_4 recorded at −196°C at the following frequencies (cm^{-1}): 769 (ν_1), 374, 362 (ν_2), a broad band at 1200–900 (ν_3), 532, 518 (ν_4). The ν_1 and ν_2 vibrations of the free tetrahedral (T_d) BF_4^- ion are inactive in the infrared spectrum. The appearance of these frequencies in the O_2BF_4 spectrum can be explained by a decrease of the symmetry of the BF_4^- ion. The O_2^+ vibration gives rise to a weak doublet in the infrared spectrum of O_2BF_4 at 1868 and 1866 cm^{-1}. The substitution of the oxygen-16 isotope by oxygen-18 leads to a shift of the doublet to 1764 and 1762 cm^{-1}. The splitting of the O_2^+ band is caused by interionic interactions in the unit cell of the crystal. The vibration frequencies of the O_2^+ ions and dioxygenyl compounds are close to that of the free ion at 1876 cm^{-1}, which confirms the existence of O_2^+ in the salts.

Reactions involving the formation and decomposition of O_2BF_4 have been investigated by the tracer atom method[92] using radioactive fluorine-18. The salt decomposes slowly at 0°C and comparatively rapidly at room temperature. O_2BF_4 specimens decompose completely in several hours in a "dynamic" vacuum but in a sealed vessel the decomposition is only partial over a period of several weeks[92]. This behaviour can be accounted for by the equilibrium

$$O_2BF_4(\text{solid}) \rightleftharpoons O_2F(\text{gas}) + BF_3(\text{gas}). \qquad (***)$$

Boron trifluoride suppresses the dissociation of O_2BF_4. Fluorine and oxygen are formed in the decomposition of O_2BF_4 by the dimolecular reaction

$$O_2F + O_2F \xrightarrow{k} F_2 + 2O_2.$$

In the experimental temperature range 0–32°C the decomposition of O_2BF_4 is described by the equation[92]

$$dp_{BF_3}/dt = kK^2/p^2_{BF_3},$$

where K is the equilibrium constant of reaction (***).

Like the dioxygenyl salts already examined, O_2BF_4 reacts with nitrogen dioxide and is hydrolysed with evolution of ozone[112]. Dioxygenyl tetrafluoroborate reacts vigorously with organic solvents but dissolves in cyanogen without reaction at −25°C.[58] Certain chemical properties of O_2BF_4 have been described by Goetschel et al.[122] When O_2BF_4 reacts with substances the ionisation potential of which is lower than that of oxygen, O_2^+ is reduced and a fluoroborate with another cation is formed. If the resulting fluoroborate is unstable, BF_3 and fluorine are evolved, i.e. O_2BF_4 can behave as a fluorinating agent. For example, O_2BF_4 reacts smoothly at −25°C with carbon tetrachloride, forming $CFCl_3$ and CF_2Cl_2. The reaction of O_2BF_4 with hexafluorobenzene yields a mixture of fluorocarbons; saturated fluorocarbons do not react with O_2BF_4. The reaction of O_2BF_4 with xenon, accompanied by evolution of O_2, takes place rapidly at −96°C and it is believed that it involves the formation of $XeBF_4$. Oxygen is evolved in the reaction of O_2BF_4 with ClO_4, Cl_2, and ClF_3. Chloryl tetrafluoroborate has been obtained by the reaction of O_2BF_4 with ClO_2.

The reaction of BF_3 with a mixture of oxygen fluorides obtained by the radiolysis of F_2 and O_2 probably results in the formation of the unstable O_6BF_4 and O_4BF_4 in addition to O_2BF_4:[58]

$$O_6F + BF_3 = O_6BF_4 \text{ (decomposes at } -140°),$$
$$O_4F + BF_3 = O_4BF_4 \text{ (decomposes at } -33°).$$

However, reliable evidence for the existence of these interesting compounds has not so far been obtained.

---o0o---

Dioxygenyl fluoro-complexes are formed by a few higher fluorides of the elements: BF_3, PF_5, AsF_5, SbF_5, BiF_5, PtF_6, and possibly SnF_4,[123] and also VF_5.[124] The stabilisation of the O_2^+ cation, i.e. the shift of the equilibrium $O_2 + X \rightleftharpoons O_2^+ + X^-$ to the right, depends significantly on the nature of X. Platinum hexafluoride, the most powerful electron acceptor, readily oxidises molecular oxygen. The Lewis acids BF_3 and EF_5 do not react with molecular oxygen but do react with O_2F radicals, which constitute a kind of "precursor" containing "almost" molecular oxygen, i.e. two oxygen atoms linked almost as strongly as in the O_2 molecule:

$$O_2F + EF_5(BF_3) \rightarrow O_2F \cdot EF_5(BF_3).$$

In this stage of the reaction, the polarisation of the O–F bond probably increases and the tendency towards the formation of a stable tetrahedral or octahedral anion induces a transfer of F^- to the environment of the central atom in the Lewis acid:

$$O_2F \cdot EF_5(BF_3) \rightarrow O_2^+EF_6^-(BF_4^-).$$

All the known dioxygenyl salts are oxidising agents, the chemical properties of which have not been investigated in sufficient detail.

REFERENCES

1. A. G. Streng, Chem. Rev., 63, 607 (1963).
2. J. J. Turner, Endeavour, 27, 42 (1968).
3. P. Allamagny, "Les Fluorures d'Oxygène", Gauthier-Villars, Paris, 1969.
4. N. Bartlett and D. H. Lohman, Proc. Chem. Soc., 115 (1962).
5. N. Bartlett, Proc. Chem. Soc., 218 (1962).
6. P. Lebeau and A. Damiens, Compt. rend., 185, 652 (1927).
7. R. A. Brown and J. J. Ligi, US P. 3367 744 (1968); C. A. 68, 70763 (1968).
8. J. A. Donohue and W. A. Wilson, US P. 3276 981 (1961); C. A., 66, 25495 (1967).
9. A. H. Borning and K. E. Pullen, Inorg. Chem., 8, 1791 (1969).
10. R. C. King and G. T. Armstrong, J. Res. Nat. Bur. Stand., A72, 113 (1968).
11. M. C. Lin and S. H. Bauer, J. Amer. Chem. Soc., 91, 7737 (1969).
12. A. R. Hilton, A. W. Jache, J. B. Beal, W. D. Henderson, and R. J. Robinson, J. Chem. Phys., 34, 1137 (1961).
13. L. Pierce, N. DiCianni, and R. H. Jackson, J. Chem. Phys., 38, 730 (1963).
14. J. W. Nebgen, F. I. Metz, and W. B. Rose, J. Mol. Spectroscopy, 21, 99 (1966).
15. E. L. Muetterties and C. W. Tullock, in "Inorganic Syntheses" (Translated into Russian), Izd. Mir, Moscow, 1967, Vol. 2.
16. E. W. Lawless and I. C. Smith, "Inorganic High-energy Oxidizers", M. Dekker Inc., New York, 1968.
17. W. B. Fox and J. S. McKenzie, US P. 3323 866 (1967); C. A., 67, 55778 (1967).
18. W. B. Fox, E. R. Eibeck, and J. S. McKenzie, US P. 3394 598 (1968).

19. R. Bougon, J. Isabey, and P. Plurien, Compt. rend., 271, 1366 (1970).
20. R. P. Nielsen, C. D. Wagner, V. A. Campanile, and J. N. Wilson, Adv. Chem. Ser., 54, 168 (1966).
21. L. V. Streng and A. G. Streng, Inorg. Chem., 4, 1370 (1965).
22. L. V. Streng and A. G. Streng, Inorg. Chem., 5, 328 (1966).
23. R. E. Staricco, J. E. Sicre, and H. J. Schumacher, Z. phys. Chem. (Frankfurt), 39, 337 (1963).
24. M. Rubinstein, J. E. Sicre, and H. J. Schumacher, Z. phys. Chem. (Frankfurt), 43, 51 (1964).
25. J. B. Levy and B. K. W. Copeland, J. Phys. Chem., 69, 3700 (1965).
26. R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, Angew. Chem., 75, 137 (1963).
27. R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, Anales Asoc. quím. argentina., 52, 167 (1964); Ref. Zhur. Khim., 8B681 (1966).
28. G. Franz and F. Neumayr, Inorg. Chem., 3, 921 (1964).
29. I. J. Solomon, A. J. Kacmarek, and J. Raney, J. Phys. Chem., 72, 2262 (1968).
30. A. Engelbrecht, E. Nachbaur, and Ch. Pupp, Monatsh., 95, 219 (1964).
31. R. F. Merritt and J. K. Ruff, J. Amer. Chem. Soc., 86, 1392 (1964).
32. R. F. Merritt and J. K. Ruff, J. Org. Chem., 30, 328 (1965).
33. J. K. Ruff and R. F. Merritt, J. Org. Chem., 30, 3968 (1965).
34. R. F. Merritt, J. Org. Chem., 30, 4367 (1965).
35. D. Soria, E. A. R. Staricco, and E. H. Staricco, Inorg. Nuclear. Chem. Letters, 5, 35 (1969).
36. L. R. Anderson and W. B. Fox, J. Amer. Chem. Soc., 89, 4313 (1967).
37. P. G. Thompson, J. Amer. Chem. Soc., 89, 4316 (1967).
38. I. J. Solomon, A. J. Kacmarek, and J. K. Raney, "5 Mezhdunarodnyi Simpozium po Khimii Ftora, Tezisy Dokladov" (Fifth International Symposium on Fluorine Chemistry. Abstracts of Reports), Moscow, 1969.
39. L. R. Anderson and W. B. Fox, Inorg. Chem., 9, 2182 (1970).
40. D. D. DesMarteau, Inorg. Chem., 9, 2179 (1970).
41. J. B. Beal, Ch. Pupp, and W. E. White, Inorg. Chem., 8, 828 (1969).
42. R. Gatti, E. Staricco, J. E. Sicre, and H. J. Schumacher, Z. phys. Chem. (Frankfurt), 35, 343 (1962).
43. L. Dauerman, E. G. Salser, and Y. A. Tajima, J. Phys. Chem., 71, 3999 (1967).
44. T. J. Malone and H. A. McGee, J. Phys. Chem., 71, 3060 (1967).
45. J. A. Blauer and W. C. Solomon, J. Phys. Chem., 72, 2307 (1968).
46. W. C. Solomon, J. A. Blauer, and F. C. Jaye, J. Phys. Chem., 72, 2311 (1968).
47. J. Troe, H. Gg. Wagner, and G. Weden, Z. Phys. Chem. (Frankfurt), 56, 238 (1967).
48. H. Henrici, M. C. Lin, and S. H. Bauer, J. Chem. Phys., 52, 5834 (1970).
49. A. Arkell, R. R. Reinhard, and L. P. Larson, J. Amer. Chem. Soc., 87, 1016 (1965).
50. A. Arkell, J. Phys. Chem., 73, 3877 (1969).
51. V. I. Vedeneev, Yu. M. Gershenzon, A. P. Dement'ev, A. B. Nalbandyan, and O. M. Sarkisov, Izv. Akad. Nauk SSSR, Ser. Khim., 1438 (1970).
52. A. G. Streng and L. V. Streng, Inorg. Nuclear. Chem., Letters, 2, 107 (1966).
53. O. Ruff and W. Menzel, Z. anorg. Chem., 211, 204 (1933).
54. A. D. Kirshenbaum and A. V. Grosse, J. Amer. Chem. Soc., 81, 1277 (1959).
55. A. V. Grosse, A. G. Streng, and A. D. Kirshenbaum, J. Amer. Chem. Soc., 83, 1004 (1961).
56. A. G. Streng and A. V. Grosse, J. Amer. Chem. Soc., 88, 169 (1966).
57. O. Ruff and Ju. Zender, Ber., 42, 1037 (1909).
58. C. T. Goetschel, V. A. Campanile, C. D. Wagner, and J. N. Wilson, J. Amer. Chem. Soc., 91, 4702 (1969).
59. J. Shamir and J. Binenboym, Inorg. Chem. Acta, 2, 37 (1968).
60. J. B. Levy and B. K. W. Copeland, J. Phys. Chem., 72, 3168 (1968).
61. O. Ruff and W. Menzel, Z. anorg. Chem., 217, 85 (1934).
62. A. D. Kirshenbaum, Inorg. Nuclear. Chem. Letters, 1, 121 (1965).
63. E. H. Staricco, J. E. Sicre, and H. J. Schumacher, Z. phys. Chem. (Frankfurt), 31, 385 (1962).
64. A. Arkell, J. Amer. Chem. Soc., 87, 4057 (1965).
65. R. D. Spratley, J. J. Turner, and G. C. Pimentel, J. Chem. Phys., 44, 2063 (1966).
66. I. V. Nikitin and V. Ya. Rosolovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1464 (1970).
67. H. J. Schumacher and P. Frisch, Z. phys. Chem., B37, (L), 1 (1937).
68. G. Brauer (Editor), "Handbuch der präparativen anorganischen Chemie" (Translated into Russian), Inostr. Lit., Moscow, 1956.
69. W. Maya, US P. 3320 147 (1967); Chem. Abst., 67, 55830 (1967).
70. K. R. Loos, C. T. Goetschel, and V. A. Campanile, Chem. Comm., 1633 (1968).
71. A. D. Kirshenbaum and A. G. Streng, J. Chem. Phys., 35, 1440 (1961).
72. T. J. Malone and H. A. McGee, J. Phys. Chem., 69, 4338 (1965).
73. A. D. Kirshenbaum, A. V. Grosse, and J. G. Aston, J. Amer. Chem. Soc., 81, 6398 (1959).
74. R. H. Jackson, J. Chem. Soc., 4585 (1962).
75. L. Pedersen, J. Mol. Structure, 3, 510 (1969).
76. K. R. Loos, C. T. Goetschel, and V. A. Campanile, J. Chem. Phys., 52, 4418 (1970).
77. P. H. Kasai and A. D. Kirshenbaum, J. Amer. Chem. Soc., 87, 3069 (1965).
78. F. E. Welsh, F. I. Metz, and W. B. Rose, J. Mol. Spectroscopy, 21, 249 (1966).
79. N. J. Lawrence, J. S. Ogden, and J. J. Turner, Chem. Comm., 102 (1966).
80. I. J. Solomon, J. K. Raney, A. J. Kacmarek, R. G. Maguire, and G. A. Noble, J. Aner, Chem. Soc., 89, 2015 (1967).
81. J. W. Nebgen, F. I. Metz, and W. B. Rose, J. Amer. Chem. Soc., 89, 3118 (1967).
82. N. J. Lawrence, J. S. Ogden, and J. J. Turner, J. Chem. Soc., A 3100 (1968).
83. I. J. Solomon, J. N. Keith, A. J. Kacmarek, and J. K. Raney, J. Amer. Chem. Soc., 90, 5408 (1968).
84. P. Frisch and H. J. Schumacher, Z. Elektrochem., 43, 807 (1937).
85. H. J. Schumacher, Trans. Electrochem. Soc., 71, 409 (1937).
86. S. W. Benson "Thermochemical Kinetics" [Wiley,

N. W., 1968] (Translated into Russian), Izd. Mir, Moscow, 1971, p. 203.
87. P. N. Noble and G. C. Pimentel, J. Chem. Phys., 44, 3641 (1966).
88. J. L. Gole and E. F. Hayes, Int. J. Quant. Chem., IIIS, 519 (1970).
89. L. Pierce, R. Jackson, and N. DiCianni, J. Chem. Phys., 35, 2240 (1961).
90. T. J. Malone and H. A. McGee, J. Phys. Chem., 70, 316 (1966).
91. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 44, 434 (1966).
92. J. N. Keith, I. J. Solomon, I. Sheft, and H. H. Hyman, Inorg. Chem., 7, 230 (1968).
93. A. G. Streng, J. Amer. Chem. Soc., 85, 1380 (1963).
94. A. V. Grosse and A. G. Streng, US P. 3320 031 (1967); Chem. Abst., 67, 75007 (1967).
95. A. G. Streng and A. V. Grosse, Adv. Chem. Ser., 36, 159 (1963).
96. A. V. Grosse and A. D. Streng, US P. 3285 842 (1966); Chem. Abst., 66, 394 92 (1967).
97. A. V. Grosse and A. G. Streng, US P. 3341 294 (1967).
98. S. I. Morrow, US P. 3377 136 (1968); Chem. Abst., 68, 106 519 (1968).
99. S. I. Morrow and A. R. Young, Inorg. Chem., 4, 759 (1965).
100. I. J. Solomon, A. J. Kacmarek, and J. Raney, Inorg. Chem., 7, 1221 (1968).
101. I. J. Solomon, A. J. Macmarek, and J. M. McDonough, J. Chem. Eng. Data, 13, 529 (1968).
102. I. J. Solomon, A. J. Kacmarek, J. N. Keith, and J. K. Raney., J. Amer. Chem. Soc., 90, 6557 (1968).
103. S. Aoyama and S. Sakuraba, J. Chem. Soc. Japan, 59, 1321 (1938); Chem. Abst., 33, 1576 (1939).
104. A. G. Streng, Canad. J. Chem., 44, 1476 (1966).
105. A. D. Kirshenbaum and A. G. Streng, J. Amer. Chem. Soc., 88, 2434 (1966).
106. N. Bartlett and D. H. Lohman, J. Chem. Soc., 5253 (1962).
107. N. K. Jha, Dis. Abs., B739 (1966).
108. N. Bartlett, Angew. Chem. (Intern. Ed.), 7, 433 (1968).
109. J. A. Ibers and W. C. Hamilton, J. Chem. Phys., 44, 1748 (1966).
110. N. Bartlett and S. P. Beaton, Chem. Comm., 167 (1966).
111. A. R. Young, T. Hirata, and S. I. Morrow, J. Amer. Chem. Soc., 86, 20 (1964).
112. I. J. Solomon, R. J. Brabets, R. K. Uenishi, J. N. Keith, and J. M. McDonough, Inorg. Chem., 3, 457 (1964).
113. A. R. Young, T. Hirata, and S. I. Morrow, US P. 3385 666 (1968); Chem. Abst., 69, 20801 (1968).
114. J. Shamir, J. Binenboym, and H. H. Claassen, J. Amer. Chem. Soc., 90, 6223 (1968).
115. J. K. Ruff, Inorg. Chem., 5, 1791 (1966).
116. A. N. Karelin, Z. K. Nikitina, Yu. Ya. Kharitonov, and V. Ya. Rosolovskii, Zhur. Neorg. Khim., 15, 941 (1970) [Russ. J. Inorg. Chem,, No. 4 (1970)].
117. P. A. W. Dean, R. J. Gillespie, R. Hulme, and D. A. Humphreys, J. Chem. Soc., A, 341 (1971).
118. Z. K. Nikitina and V. Ya. Rosolovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2173 (1970).
119. V. I. Belova, V. Ya. Rosolovskii, and Z. K. Nikitina, Zhur. Neorg. Khim., 16, 1457 (1971) [Russ. J. Inorg. Chem., No. 5 (1971)].
120. V. I. Belova, Ya. K. Syrkin, D. V. Bantov, and V. F. Sukhoverkhov, Zhur. Neorg. Khim., 13, 1457 (1968) [Russ. J. Inorg. Chem., No. 5 (1968)].
121. K. R. Loos, V. A. Campanile, and C. T. Goetschel, Spectrochim. Acta, 26A, 365 (1970).
122. C. T. Goetschel, V. A. Campanile, C. D. Wagner, and J. N. Wilson, Amer. Chem. Soc., Prepr., 12, 98 (1968); Chem. Abst., 71, 119 173 (1969).
123. D. V. Bantov, V. F. Sukhoverkhov, and Yu. N. Mikhailov, Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 2, Issue 1, 84 (1968).
124. I. J. Solomon, U. S. Govt. Res. Develop. Rep., 69, (8), 62 (1969); Chem. Abst., 71, 18 410 (1969).

Institute of New Chemical Problems, USSR Academy of Sciences, Chernogolovka, Moscow Region