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SECOND ANNUAL PROGRESS REPORT
FOR THE
OFFICE OF NAVAL RESEARCH
Contract Nonr 3085(01)

ADDITION AND SUBSTITUTION
PRODUCTS OF OXYGEN FLUORIDES

A. G. Streng and A. V. Grosse
January 19, 1962

The Research Institute of Temple University
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Philadelphia 44, Pennsylvania
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>SUMMARY</strong></td>
<td>1a</td>
</tr>
<tr>
<td><strong>I. A NEW TYPE OF HIGHLY COLORED ADDITION PRODUCTS OF DIOXYGEN DIFLUORIDE</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>II. THE O₂F₂ + ClF REACTION. FORMATION OF O₂ClF₃</strong></td>
<td>3</td>
</tr>
<tr>
<td>A. Reaction Conditions</td>
<td>3</td>
</tr>
<tr>
<td>B. Solvents for the Reagents and the Reaction Products</td>
<td>9</td>
</tr>
<tr>
<td>C. Formation of an Unknown Blue Compound or Compounds</td>
<td>10</td>
</tr>
<tr>
<td>D. Synthesis of the Violet Compound directly From O₂ and ClF₃ Under the Influence of Ultraviolet Light</td>
<td>11</td>
</tr>
<tr>
<td><strong>III. THE PROPERTIES OF THE VIOLET O₂F₂ + ClF ADDITION PRODUCT</strong></td>
<td>12</td>
</tr>
<tr>
<td>A. General</td>
<td>12</td>
</tr>
<tr>
<td>B. Solubility</td>
<td>14</td>
</tr>
<tr>
<td>C. Conductivity</td>
<td>15</td>
</tr>
<tr>
<td>D. Visible Spectrum</td>
<td>17</td>
</tr>
<tr>
<td><strong>IV. CHEMICAL REACTIONS OF O₂ClF₃ AT LOW TEMPERATURES</strong></td>
<td>20</td>
</tr>
<tr>
<td>A. Reaction with Ammonia</td>
<td>20</td>
</tr>
<tr>
<td>B. Reaction with Methane</td>
<td>22</td>
</tr>
<tr>
<td>C. Reaction with Ethane</td>
<td>22</td>
</tr>
<tr>
<td>D. Reaction with Ethylene</td>
<td>22</td>
</tr>
<tr>
<td>E. Reaction with Hydrogen</td>
<td>23</td>
</tr>
<tr>
<td>V. REACTION OF O$_2$F$_2$ WITH BrF$_3$ AND SF$_4$</td>
<td>25</td>
</tr>
<tr>
<td>A. The O$_2$F$_2$ + BrF$_3$ Reaction</td>
<td>25</td>
</tr>
<tr>
<td>B. The O$_2$F$_2$ + SF$_4$ Reaction</td>
<td>26</td>
</tr>
<tr>
<td>C. Irradiation of SF$_4$ + O$_2$ with Ultraviolet Light</td>
<td>29</td>
</tr>
<tr>
<td>VI. CHEMICAL BEHAVIOR OF O$_2$F$_2$ WITH FLUORIDES OF ELEMENTS CLOSE TO OXYGEN AND FLUORINE IN THE PERIODIC SYSTEM</td>
<td>30</td>
</tr>
<tr>
<td>A. The Reaction of O$_2$F$_2$ with PF$_3$</td>
<td>30</td>
</tr>
<tr>
<td>B. The Reaction of O$_2$F$_2$ with IF$_5$</td>
<td>31</td>
</tr>
<tr>
<td>C. The Reactions of O$_2$F$_2$ with SiF$_4$ and CF$_4$</td>
<td>31</td>
</tr>
<tr>
<td>D. The Reaction of O$_2$F$_2$ with N$_2$F$_4$</td>
<td>32</td>
</tr>
<tr>
<td>VII. EXPERIMENTS IN A U-SHAPE ELECTRICAL-DISCHARGE TUBE</td>
<td>35</td>
</tr>
<tr>
<td>VIII. REMARKS ON HYDROGEN SUPEROXIDE, H$_2$O$_4$</td>
<td>39</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>41</td>
</tr>
<tr>
<td>THE REAGENTS USED</td>
<td>42</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Visible Spectrum of Violet Product</td>
<td>19</td>
</tr>
<tr>
<td>2.</td>
<td>Solubility of SF₆ and ClF₃ in ClO₃F</td>
<td>28</td>
</tr>
<tr>
<td>3.</td>
<td>The U-Shape Discharge Tube</td>
<td>36</td>
</tr>
<tr>
<td>A-1.</td>
<td>The Apparatus for Preparation of O₂F₂</td>
<td>43</td>
</tr>
<tr>
<td>A-2.</td>
<td>Reaction Vessel for Preparation of O₂F₂</td>
<td>44</td>
</tr>
<tr>
<td>A-3.</td>
<td>Reaction Vessel for Preparation of O₃F₂</td>
<td>47</td>
</tr>
</tbody>
</table>
INTRODUCTION

This is the Second Annual Report for the Office of Naval Research, Contract Nonr 3085(01). It covers the period from January 1 to December 31, 1961.

The research program was specified by the Research and Development Task Order and consists of the two following subjects:

I. The synthesis and characterization of the oxygen fluorides.

II. The synthesis and characterization of certain substitution and addition products of the oxygen fluorides.
SUMMARY

A new type of highly colored deep-violet addition compounds of dioxygen difluoride has been obtained. These compounds are formed by addition to ClF, BrF₃ and SF₄, under mild reaction conditions. They have a remarkable oxidizing power, even at very low temperatures.

The analogous fluorides of the other elements adjoining oxygen and fluorine in the Periodic System, namely, N₂F₄, PF₃, SiF₄, CF₄ and IF₅, did not form addition compounds of this type.

The O₂F₂ + ClF reaction was studied extensively. Various combinations of the factors influencing the synthesis were investigated, and the yield of the violet addition product was raised to 81% of the theoretical value.

The investigation of the properties of the violet compound, the elementary composition of which was found to be O₂ClF₃, showed that the solid violet compound, contaminated only by ClF₃, is stable at 195⁰K. At this temperature it was kept for over 9 months without any noticeable decomposition. The compound is soluble in liquid ClF₃, ClF, O₂F₂ and HF, at 125-190⁰K., but is insoluble in liquid O₂, O₃, ClO₃F, C₃F₈, NF₃, CCl₂F₂ and CClF₃ in the range of 90-160⁰K. The solutions are less stable than the solid compound. The measurements of the electrical conductivity of a solution of the violet compound in anhydrous HF at -78⁰C. showed that O₂ClF₃ is not an electrolyte.
The study of the reactivity of the violet compound at low temperatures showed its extremely high oxidizing power. The compound reacts vigorously with ammonia, ethane and ethylene, even at 120-160°C. There was no reaction, however, with liquid methane at 90°C.; with gaseous methane at 150°C.; and with gaseous hydrogen at 120°C. under a pressure of 100 mm. Hg.

The violet addition product was synthesized also from ClF3 and O2 at 195°C. under pressure, by irradiation with ultraviolet light. The preliminary data on the visible absorption spectrum of this compound were obtained.

The decomposition of a solution of O2ClF3 in anhydrous HF led, under some conditions, to the formation of a blue compound or compounds. The nature of these compounds was not established.

The flow diagram and the description of the methods of preparation of O2F2 and O3F2 are given.
I. A NEW TYPE OF HIGHLY COLORED ADDITION PRODUCTS OF DIOXYGEN DIFLUORIDE

The reactions of oxygen fluorides with various lower fluorides of the elements close to oxygen and fluorine in the Periodic System were studied. It was found that at low temperatures, i.e. 110-140°C, dioxygen difluoride, \( \text{O}_2\text{F}_2 \), adds chlorine monofluoride, \( \text{ClF} \), forming a highly colored, purple to violet, addition compound. The elementary formula of this compound is \( \text{O}_2\text{ClF}_3 \). This is a new type of compound with remarkable oxidizing properties.

Bromine trifluoride, \( \text{BrF}_3 \), and sulfur tetrafluoride, \( \text{SF}_4 \), also form, under very mild conditions, highly colored brown-to-violet addition products.

The fluorides of the other elements close to oxygen and fluorine in the Periodic System, namely, nitrogen, phosphorus, carbon and silicon do not form the violet addition compounds. Phosphorus trifluoride, \( \text{PF}_3 \), combines with \( \text{O}_2\text{F}_2 \), forming \( (\text{POF}_3)_n \) and \( \text{PF}_5 \). The \( \text{POF}_3 \) is produced in the form of an interesting polymer which depolymerizes at higher temperatures to gaseous \( \text{POF}_3 \). Tetrafluorohydrazine, \( \text{N}_2\text{F}_4 \), reacts, giving \( \text{O}_2 \) and \( \text{NF}_3 \). Carbon tetrafluoride, \( \text{CF}_4 \), and silicon tetrafluoride, \( \text{SiF}_4 \), do not react, as was expected, in view of their saturated nature. Iodine pentafluoride, \( \text{IF}_5 \), does not react at low temperatures but under more drastic conditions will probably form iodine heptafluoride, \( \text{IF}_7 \).
II. THE $\text{O}_2\text{F}_2 + \text{ClF}$ REACTION. FORMATION OF $\text{O}_2\text{ClF}_3$

A. Reaction Conditions

At 90$^\circ$K., solid dioxygen difluoride (m.p. 109.7$^\circ$K.) and solid chlorine monofluoride (m.p. 119$^\circ$K.) do not react when ClF is condensed on a thin solidified layer of $\text{O}_2\text{F}_2$.

Gaseous $\text{O}_2\text{F}_2$, on the other hand, at about 195$^\circ$K., reacts with ClF directly to give oxygen gas and ClF$_3$, without the formation of intermediate compounds. The reaction proceeds in accordance with the equation:

$$\text{O}_2\text{F}_2 + \text{ClF} \rightarrow \text{O}_2 + \text{ClF}_3 \quad -30.1 \text{ Kcal}.$$  

At temperatures of about 110-140$^\circ$K., however, $\text{O}_2\text{F}_2$ reacts with ClF, forming a deep violet intermediate addition compound, $\text{O}_2\text{ClF}_3$. The formation of the violet compound is usually accompanied by the evolution of gaseous oxygen and fluorine in varying ratios. At temperatures above 140$^\circ$K., the reaction proceeds violently. The ClF abstracts the fluorine from $\text{O}_2\text{F}_2$ according to equation (1). If the addition of ClF is too rapid, some of the $\text{O}_2\text{F}_2$ is decomposed to $\text{O}_2$ and F$_2$.

At more moderate temperatures (110-140$^\circ$K.) and with a slow addition of ClF, three reactions take place simultaneously in varying proportions.
The formation of the violet addition product:

\[ O_2F_2 + ClF \rightarrow O_2ClF_3 \]  \hspace{1cm} (1)

The decomposition of the violet compound either at the time of formation or when the temperature is raised:

\[ O_2ClF_3 \rightarrow O_2 + ClF_3 \]  \hspace{1cm} (2)

and the thermal decomposition of \( O_2F_2 \):

\[ O_2F_2 \rightarrow O_2 + F_2 \]  \hspace{1cm} (3)

The extent of each reaction can be readily determined analytically, since reactions (2) and (3) produce gaseous oxygen and reaction (3), produces, in addition, free fluorine. The oxygen can be determined by standard Orsat analysis or other known methods; the fluorine by Hg-burette absorption; and the chlorine trifluoride by freezing it out (m.p. 190°K.) and checking its purity by vapor-pressure measurement, infrared spectrum or melting point.

Reaction (1) is difficult to control. Much effort was exerted to find the conditions necessary to minimize reactions (2) and (3); i.e., to increase the yield of the violet product.

Since the violet reaction product is energy rich, it decomposes rapidly if the reaction proceeds too violently or even under mild conditions, if impurities are present. In the presence of traces of water, nitrogen oxides or nitrogen oxyfluorides, the violet compound decomposes quickly or does not form.

In view of the intense color it was at first thought that ozone was formed, possibly following the equation:
3 O₂F₂ + 3 ClF → 2 O₃ + 3 ClF₃

Although ozone is deep blue and the reaction product violet-blue, ozone and liquid O₂F₂ form a violet-blue solution.

It was found, however, that O₃ does not dissolve in ClF₃ and does not form an addition product with it. In the absence of O₂F₂ and in the presence of ClF₃, ozone, as expected, retains its characteristic deep blue color. Ozone can be isolated easily from such a mixture by two methods: (1) by extraction with liquid O₂, which immediately gives a deep blue solution, while ClF₃ remains practically insoluble, or (2) by high-vacuum distillation. At a total pressure of 12μ and at a temperature of 158⁰K., the violet compound does not distil. Ozone, on the other hand, has a vapor pressure of 600 mm. at 158⁰K. and would readily distil.

The violet reaction product may be prepared simply by adding pure ClF to pure O₂F₂. The dioxygen difluoride is condensed in a reaction tube cooled in a liquid-oxygen bath, the ClF is added and the tube is warmed slowly. In the temperature range of about 110 to 140⁰K., these compounds react, forming, together with other compounds, the intense violet addition product, which has strong oxidizing properties. The most favorable temperature is 119⁰K., the melting point of ClF.
The yield of the violet compound depends upon the rate of addition of ClF, temperature, area and uniformity of distribution of O₂F₂.

The three reactions mentioned previously take place simultaneously. The optimum yield attained was about 50%, based on reaction (1), although in most cases the yield was very much smaller.

The simplest way to increase the yield is to dilute the reagents. Freon 13 (CClF₃) was found to be a solvent for O₂F₂ at about 130°. When gaseous ClF diluted with helium is bubbled through a solution of O₂F₂ in Freon 13, cooled to 130-140°K., the reaction between O₂F₂ and ClF proceeds in most cases without gas evolution; i.e., without decomposition of the violet compound into O₂ and ClF₃, according to reaction (2), or without decomposition of O₂F₂ into O₂ and F₂, as in reaction (3). It was found, however, that in the presence of Freon 13, the thermal stability of the violet compound is substantially decreased. The violet compound is not soluble in Freon 13; it precipitates to the bottom of the reaction vessel and decomposes with considerable velocity at about 195°K. It may be that impurities in Freon 13 cause this decomposition.

There was no formation of a violet compound at all when Freon 12 (CCl₂F₂) was used as the solvent for O₂F₂. The synthesis
was attempted with a 6.3 wt.% O$_2$F$_2$ solution in Freon 12. The solution was cooled to 90$^\circ$K., ClF was added and the tube was slowly warmed up. The reaction between O$_2$F$_2$ and ClF started at about 130$^\circ$K., but without the formation of a violet product.

The use of perchloryl fluoride as the solvent in the reaction between O$_2$F$_2$ and ClF did not increase the yield of the violet compound but did serve to lower its stability. A 14.0 wt.% O$_2$F$_2$ solution in ClO$_3$F was used. The solution was cooled to 90$^\circ$K. and small portions of ClF gas were added. After each addition, the reaction vessel was warmed to 125$^\circ$K. A slow reaction occurred, with the formation of a comparatively large amount of ClF$_3$ and a comparatively small amount of the violet product. Both these products are insoluble in ClO$_3$F at 125$^\circ$K. and collect on the bottom of the vessel. The vessel was then cooled again to 90$^\circ$K. and a new portion of ClF was added. When all the O$_2$F$_2$ was consumed, the reaction vessel was slowly warmed to 190$^\circ$K. At this temperature, ClF$_3$ dissolves completely in ClO$_3$F and the violet compound remains on the bottom in the form of dark violet flakes. The yield of the violet compound was much smaller than that obtained in the reaction between pure O$_2$F$_2$ and ClF. At about 195$^\circ$K. the violet compound decomposed completely.

Anhydrous hydrogen fluoride, HF, is also a good solvent for both O$_2$F$_2$ and the violet compound. At its melting point, 190$^\circ$K., hydrogen fluoride dissolves about 23 mole % O$_2$ClF$_3$, forming a deep
violet solution. A difficulty arises, however, from the fact that
the solution of the violet compound in HF is stable at 190-195°K.,
only under an oxygen pressure of about two atmospheres. For this
reason the removal of HF and the isolation of the violet compound
are complicated.

The attempts to lower the melting point of HF by the
addition of KF\(^1\) and thereby to increase the stability of the
solutions of the violet compound, gave no improvement. On the
contrary, in the presence of KF the solutions of the violet compound
in HF lost their color much faster than normally, most probably owing
to the formation of K(CIF\(_4\)).

Perfluoropropane, C\(_3\)F\(_8\) (m.p. 90°K., b.p. 235°K.), was also
investigated as a diluent for the O\(_2\)F\(_2\) + ClF reaction. It dissolves
over 33 wt.% ClF at 150°K. and mixes homogeneously with it at 160°K.
The solubility of O\(_2\)F\(_2\) in C\(_3\)F\(_8\), however, is very low.

Perfluoropropane used as a diluent increased the yield
of the violet compound up to 81% of theory. The violet compound
and ClF\(_3\) are, however, not soluble in C\(_3\)F\(_8\). The stability of the
violet product in the presence of C\(_3\)F\(_8\) was found to be low.

B. Solvents for the Reagents and the Reaction Products

The effort is continuing to find a suitable solvent for the reagents, $O_2F_2$ and $ClF$, and for the reaction products, in order to facilitate the isolation of the pure violet compound.

Hildebrand's generally useful concept of solubility parameters does not always predict correctly the solubility behavior of liquefied gases at low temperatures. It was, therefore, necessary to obtain miscibility and solubility information experimentally.

The substances tested and the results obtained to date are as follows:

<table>
<thead>
<tr>
<th>Mixes homogeneously with:</th>
<th>Forms two practically insoluble layers with:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2F_2$:</td>
<td></td>
</tr>
<tr>
<td>$O_3F_2$ at 116°C</td>
<td>$N_2$ at 77°C</td>
</tr>
<tr>
<td>$CCl_2F_2$ at 116</td>
<td>$F_2$ at 77</td>
</tr>
<tr>
<td>$CClF_3$ at 116</td>
<td>$CF_4$ at 90</td>
</tr>
<tr>
<td>$CO_3F$ at 127</td>
<td>$O_2$ at 90</td>
</tr>
<tr>
<td>$ClF_3$ at 180</td>
<td>$NF_3$ at 130</td>
</tr>
<tr>
<td>$NO_2F$ at 195</td>
<td>$C_3F_8$ at 140</td>
</tr>
<tr>
<td></td>
<td>$N_2F_4$ at 130</td>
</tr>
<tr>
<td>$ClF$:</td>
<td></td>
</tr>
<tr>
<td>$CO_3F$ at 160°C</td>
<td>$O_3F_2$ at 90°C</td>
</tr>
<tr>
<td>$C_3F_8$ at 160</td>
<td>$NF_3$ at 150</td>
</tr>
<tr>
<td></td>
<td>$ClF_3$ at 174</td>
</tr>
<tr>
<td></td>
<td>$HF$ at 173</td>
</tr>
<tr>
<td>$ClF_3$:</td>
<td></td>
</tr>
<tr>
<td>$O_2F_2$ at 180°C</td>
<td>$O_3F_2$ at 90°C</td>
</tr>
<tr>
<td>$ClO_3F$ at 195</td>
<td>$NF_3$ at 140</td>
</tr>
<tr>
<td>$HF$ at 195</td>
<td>$ClF$ at 174</td>
</tr>
<tr>
<td></td>
<td>$CCl_2F_2$ at 125</td>
</tr>
<tr>
<td></td>
<td>$CClF_3$ at 190</td>
</tr>
<tr>
<td></td>
<td>$C_3F_8$ at 235</td>
</tr>
</tbody>
</table>


In the course of these investigations it was found also that:

1) \( \text{O}_2\text{F}_2 \) dissolves about 20 wt.% of \( \text{SiF}_4 \) at 150\(^\circ\)K.
   and about 11 wt.% of HF at 186\(^\circ\)K.

2) HF dissolves at least 6.6 mole % \( \text{ClF} \) at 190\(^\circ\)K.
   and about 5.8 wt.% \( \text{O}_2\text{F}_2 \) at 176\(^\circ\)K. and 11.6 wt.% \( \text{O}_2\text{F}_2 \) at 186\(^\circ\)K.

3) FC-15 (\( \text{C}_8\text{F}_{16}\text{O} \)) dissolves about 3 wt.% \( \text{ClF}_3 \) at 195\(^\circ\)K.

4) \( \text{C}_3\text{F}_8 \) dissolves some \( \text{O}_2\text{F}_2 \) at 130\(^\circ\)K.

5) \( \text{N}_2\text{F}_4 \) dissolves some \( \text{O}_2\text{F}_2 \) at 140\(^\circ\)K.

---

C. Formation of an Unknown Blue Compound or Compounds

If the violet compound is warmed up to about 140\(^\circ\)K. in the presence of \( \text{ClF} \) and \( \text{ClF}_3 \), it changes into a greenish-blue compound, which exists only over a very narrow temperature range. The greenish-blue compound dissolves in \( \text{ClF} \) at about 125-130\(^\circ\)K., to form a greenish-blue solution, but the color disappears in about three to five minutes. Probably another blue compound was formed while pumping off the oxygen from a violet solution of \( \text{O}_2\text{ClF}_3 \) in anhydrous HF at 190-195\(^\circ\)K. The solution changed color and became deep blue like the color of ozone. The question might well be raised whether in the decomposition of \( \text{O}_2\text{ClF}_3 \) the oxygen is liberated as \( \text{O}_3 \) or whether a new type of compound is formed which has a color similar to that of ozone. This possibility will be checked later by
determining the visible absorption spectrum of the solution.

It is of interest to mention here that over 3.5 wt.% of ozone dissolves in HF at 195°K. and at pressures less than one atmosphere to form a solution similar in appearance to the one described above.

D. Synthesis of the Violet Compound Directly From O₂ and ClF₃ Under the Influence of Ultraviolet Light

The discovery that oxygen pressure has an important effect on the stability of the violet compound dissolved in HF, led us to the experiment described below.

Pure ClF₃ was placed in a quartz tube surrounded by dry ice, i.e., at 195°K., and irradiated with ultraviolet light, principally at 2537 Ångstrom units with an intensity of 7 milliwatts/cm². Under a pressure of two atmospheres of oxygen a violet compound was produced after only a few seconds irradiation; the color increased appreciably with time. On the other hand, if the pressure of the oxygen was only 15 mm. the violet compound was not formed. A check experiment on pure ClF₃ in the absence of oxygen showed no change in color. Thus, at the present time we have a reversible reaction for the formation of the violet compound from the simple, commercially available materials, O₂ and ClF₃, merely by changing the pressure of the oxygen.
III. THE PROPERTIES OF THE VIOLET $\text{O}_2\text{F}_2 + \text{ClF}$ ADDITION PRODUCT

A. General

From classical theories of structure of inorganic chemistry, and a knowledge of the structure of $\text{O}_2\text{F}_2$ certain simple structures of the new compound may be postulated. The structure of $\text{O}_2\text{F}_2$ has been determined to be:

$$\text{F} - \text{O} - \text{O} - \text{F}.$$ 

Since the chlorine in $\text{ClF}$ is monovalent and can be converted to trivalent chlorine, the simplest assumption is that the addition of $\text{ClF}$ to $\text{F} - \text{O} - \text{O} - \text{F}$ takes place either (a) across the $\text{O} - \text{F}$ bond, leading to the compound:

$$\text{F} \quad \text{Cl} \quad \text{O} - \text{O} - \text{F}$$

or (b) across the $\text{O} - \text{O}$ bond, leading to the compound:

$$\text{F} - \text{O} - \text{Cl} - \text{O} - \text{F}$$

In case (a), the addition of a second molecule of $\text{ClF}$ would lead to the compound:

$$\text{F} \quad \text{Cl} - \text{O} - \text{O} - \text{Cl}$$
In the less likely case of addition of the second molecule across the O - O bond the isomeric compound

$$\begin{array}{c}
\text{Cl} - \text{O} - \text{Cl} - \text{O} - \text{F} \\
\text{F} \\
\text{F}
\end{array}$$

would be obtained.

The latter compound could also add a third molecule of ClF leading to the compound:

$$\begin{array}{c}
\text{Cl} - \text{O} - \text{Cl} - \text{O} - \text{Cl} - \text{F} \\
\text{F} \\
\text{F}
\end{array}$$

Either of the alternatives (a) and (b) is possible, because the bond strengths F - O - and O - O - are not very different. They are estimated to be 61 Kcal. for O - O - and 50 Kcal for F - O -, assuming a chain structure in O$_2$F$_2$.

The following properties of the compound have been determined so far:

The color is close to that of a 0.1% aqueous solution of the intense violet dye methyl violet. It is solid at 195°K. and in the absence of impurities can be kept at this temperature for months without noticeable decomposition. The thermal stability of the compound depends on the presence of catalysts or inhibitors of decomposition. It was found that if the original O$_2$F$_2$ contains nitrogen compounds
such as NOF, NO$_2$F, or NO$_2$ or other oxides of nitrogen, the decomposition of the violet compound is catalyzed so that the yields are very poor and the thermal stability is low.

The vapor pressure of the violet reaction product at 158°K. is below 12 microns.

The following observations were also made: If the O$_2$F$_2$ + ClF reaction is carried out with an excess of ClF or in the presence of ClO$_3$F or Freons 12 and 13 as diluents, the yield of the violet compound is low.

The violet compound is stable at temperatures up to 195°K. and has been kept at this temperature for 9 months. In general it was found that the stability of dry solid violet product is much higher than its stability in the dissolved state.

It was noted that the violet compound does not distil at 160°K. even at a pressure of 12 microns. It was found, however, that under these conditions it dissociates into O$_2$F$_2$ and ClF, which were recovered in a liquid-nitrogen trap. If these dissociation products are warmed to about 130°K. the deep violet compound forms again.

B. Solubility

The search for a suitable solvent for the O$_2$F$_2$ + ClF violet reaction product continues. The following substances have been
tested, and the results obtained to date are listed below:

The violet compound is soluble in:

liquid ClF at 125°K.
" O₂F₂ at 140
" ClF₃ at 190
" HF at 190

The stability of all these solvents is lower than the stability of the violet compound in the solid state.

The violet compound is not soluble in:

liquid O₂ at 90°K.
" O₃ at 90
" ClO₃F at 135
" C₃F₈ at 140
" NF₃ at 150
" CCl₂F₂ at 160
" CClF₃ at 160

C. Conductivity

The electrolytic conductivity of a solution of the violet compound in HF was measured by using a Wheatstone bridge*
and a specially made Teflon cell with platinum electrodes.

A 0.5-molar solution of $O_2ClF_3$ in HF was investigated at 195°C. The anhydrous HF had a specific conductivity of $3.57 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$. The conductivity of the violet solution was $3.33 \times 10^{-3}$ and changed upon standing for an hour to $3.57 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$. After this change, the violet compound was permitted to decompose by pumping off the oxygen, and the residual clean colorless solution of ClF$_3$ in HF had a conductivity of $3.57 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$. The best data on the specific conductivity of pure HF indicate that our HF contained traces of water in the amount of 2 mg. per liter.$^4$

It is obvious that our violet compound does not increase the specific conductivity of anhydrous HF and is consequently not an electrolyte. In contrast, a 0.5-molar solution of a typical electrolyte, namely, KF in HF, has a specific conductivity of 86.0 ohm$^{-1}$ cm$^{-1}$. Thus, a similar concentration of potassium fluoride conducts the current approximately 25,000 times better than does our violet compound. The possibility that our violet compound, $O_2ClF_3$, might be ionic or salt like, dissociating for example into the ions, 

$$(O_2ClF_2)^+ + F^-,$$

is excluded.

---

D. Visible Spectrum

It was previously reported that the violet compound is also formed when liquid ClF₃ (in the presence of oxygen at 195⁰K.) is irradiated with ultraviolet light. The visible spectrum of this compound was taken.

The violet compound was prepared for this investigation directly in a specially made silica-glass spectroscopic cell. The cell was filled with ClF₃ to about two-thirds of its capacity and gaseous O₂ (two atmospheres pressure) was added. The cell was then exposed for 15-20 min. at 195⁰K. to ultraviolet light of 2537Å units and an intensity of 7 milliwatts/cm².

The spectrum was taken on a Beckman spectrophotometer, Model DU, fitted with a special cell compartment for measurements at low temperatures.³

The preliminary data obtained are given in Table I and Fig. 1.
TABLE I

Preliminary Data on Visible Spectrum of Violet Compound Formed by ClF₃ + O₂ Under Ultra-Violet Light at 1950K.

<table>
<thead>
<tr>
<th>Wave length, m</th>
<th>Transmittance, %</th>
<th>Estimated molar extinction coefficient, cm⁻¹ mole⁻¹ lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>96</td>
<td>--</td>
</tr>
<tr>
<td>475</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>500</td>
<td>69</td>
<td>--</td>
</tr>
<tr>
<td>550</td>
<td>59</td>
<td>46</td>
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<tr>
<td>600</td>
<td>66</td>
<td>--</td>
</tr>
<tr>
<td>650</td>
<td>57</td>
<td>49</td>
</tr>
<tr>
<td>700</td>
<td>67</td>
<td>--</td>
</tr>
<tr>
<td>750</td>
<td>96</td>
<td>--</td>
</tr>
<tr>
<td>850</td>
<td>88</td>
<td>--</td>
</tr>
<tr>
<td>900</td>
<td>84</td>
<td>--</td>
</tr>
</tbody>
</table>

The concentration of the solution used was estimated to be about 0.005 mole/lit.
IV. CHEMICAL REACTIONS OF $O_2ClF_3$ AT LOW TEMPERATURES

It was found that dioxygen monochlorotrifluoride, $O_2ClF_3$, is highly reactive at low temperatures towards ammonia and various hydrocarbons. In this respect it is similar to the highly reactive ozone, which was found to react even at 150-160°K. with ammonia. Usually no chemical reactions take place at a temperature range of 100-150°K. outside of exceptionally reactive systems; for example, free atoms or radicals, as has been strikingly demonstrated by Dr. H. Broida and his associates at the National Bureau of Standards.

Since $O_2ClF_3$ is of interest as a potential oxidizer, it was of importance to study its reactions with various hydrides.

A. Reaction with Ammonia

It was established in preliminary experiments, that gaseous ammonia entering a reaction vessel which contains the deep-violet $O_2ClF_3$, at a temperature of 90°K., reacts violently with a flash, forming some white solids and some nitrogen-containing gases, while the violet color disappears.

(5) Grosse, A. V., and Streng, A. G., Technical Note No. 4, Contract No. AF 18(600)-1475, Project No. 7-7968, the Research Institute of Temple University, August 1, 1957.
If the ammonia is condensed first in the upper part of the reaction tube cooled to 90°K., then the reaction proceeds slowly as the vessel is warmed up to 150-160°K. Ammonia has a vapor pressure of about 1 mm. at 160°K. and therefore evaporates slowly and reacts as a gas with the solid violet compound. Under these conditions the reaction proceeds smoothly without any gas evolution. The violet color disappears and a white solid is formed.

Ammonium fluoride and other ammonium salts, HF, HCL, and the oxy-acids of chlorine (either free or as ammonium salts) were identified among the reaction products.

Hydrogen fluoride was identified by vacuum distillation, formation of NaF. HF and titration. Hydrogen chloride was identified through formation of silver chloride. Ammonia was determined quantitatively by Kjeldahl's method. The oxynitrogen acids or oxychlorine acids were identified qualitatively by Lunge's reagent. Anions of the oxychlorine acids, i.e., chlorite, chlorate or perchlorate, were identified by reduction with zinc to chloride ion.

In one experiment 0.25 g. O₂ClF₃ was reacted with about 0.10 g. of ammonia. 52 mg. of NH₃ was found in the reaction product together with about 3 mg. of N₂ (gas). Thus, about one-half of the ammonia added formed ammonium salts. This mixture of ammonium salts and oxidizers is potentially dangerous and can detonate!
B. Reaction with Methane

Dioxygen monochlorotrifluoride does not react with an excess of liquid methane at 900K. It also does not react with gaseous methane at a pressure of 100 mm. Hg at 1500K. During one hour there was neither a decrease in pressure nor a disappearance of the violet color.

C. Reaction with Ethane

In contrast with the observations in the case of methane, ethane, when admitted to the violet compound at a temperature of 1400K., reacted immediately. The violet color disappeared and white solids were formed but no gas was evolved. That is, there was no formation of O₂, F₂ or CO.

Hydrogen fluoride was identified in the reaction products as was ClF₃, which was present as a contaminant in the original O₂ClF₃.

D. Reaction with Ethylene

The reaction vessel containing 1.39 g. of O₂ClF₃ was cooled to 1200K. and ethylene gas was introduced (ethylene has a vapor pressure of about 1.0 mm. Hg at 1200K.) in portions of about 5 mg. at a rate of about 1 mg. per sec. After an interruption of one to two minutes, new portions were added.
Under those conditions ethylene reacted immediately, causing decolorization of the violet compound and formation of the white solid products, while no measurable gas evolution, i.e. no formation of \( \text{O}_2 \), \( \text{F}_2 \) or \( \text{CO} \), took place.

On one occasion when ethylene was added at a higher rate, the reaction proceeded with a flame which extinguished itself as soon as the ethylene flow was stopped. A total of 0.179 g. of ethylene was added to 1.3 g. of \( \text{O}_2\text{ClF}_3 \); the temperature of the bath after this addition was slowly raised at the rate of \( 1-1\frac{1}{2}^\circ/\text{min.} \) No gas evolution was noticed up to \( 140^\circ\text{K.} \) At \( 140^\circ\text{K.} \) a violent explosion took place, shattering the reaction vessel and a large part of the reaction system. Evidently, intermediate or partly oxidized products were formed.

In all reactions of \( \text{O}_2\text{ClF}_3 \) with hydrogen-containing substances, HF is the most likely reaction product. Carbonyl fluoride, \( \text{COF}_2 \) and other intermediate oxyfluorides, for example, oxalyl fluoride, \( \text{C}_2\text{O}_2\text{F}_2 \), may be formed. In view of the violent explosion which took place, it is also likely that some C-H containing compounds were present.

E. Reaction with Hydrogen

During one hour at 90-120\(^\circ\text{K.} \), there was no reaction between \( \text{O}_2\text{ClF}_3 \) and hydrogen gas at a pressure of 100 mm. Hg. Any reaction
would be easily noticeable by disappearance or change of the violet color or a decrease in the pressure of hydrogen.

The nonreactivity of $\text{O}_2\text{ClF}_3$ with hydrogen and methane parallels the chemical properties of ozone. We have shown earlier that pure (100%) ozone can be mixed at $-78^\circ\text{C.}$ and even at room temperature with hydrogen and methane without reaction.\(^6,7\) (The mixture $1.5 \text{CH}_4 + 2\text{O}_3$, at 804 mm. Hg., showed at $+21^\circ\text{C.}$ a pressure increase of 26 mm. Hg. on standing for 1.0 hour).

From the present preliminary evidence it is likely that $\text{O}_2\text{ClF}_3$ will be more reactive than ozone at low temperatures.


V. REACTION OF $O_2F_2$ WITH BrF$_3$ AND SF$_4$

The lower fluorides of bromine and sulfur, BrF$_3$ and SF$_4$, under very mild conditions may also form highly colored addition products with $O_2F_2$, although the compounds so far made seem to have only a transitory existence. The reactions are not always reproducible. Silicon tetrafluoride, SiF$_4$, interferes with the formation of the addition products.

A. The $O_2F_2 + BrF_3$ Reaction

The bromine analog of ClF, bromine trifluoride, BrF$_3$, also reacts with $O_2F_2$.

If liquid BrF$_3$ cooled to its melting point, 282°K., is dropped onto solid $O_2F_2$ cooled to 90°K., a spontaneous reaction occurs with evolution of heat and gas. Analysis of the reaction products showed that the reaction proceeds in accordance with the equation:

$$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2 -56.7 \text{ Kcal.}$$

Under milder conditions, a brown-violet compound may be formed. The reaction proceeds, analogously to the ClF reaction, according to the equation:

$$O_2F_2 + BrF_3 \rightarrow O_2F_2 \cdot BrF_3.$$
Bromine trifluoride was condensed on the walls of the reaction vessel at 90°K. A thin layer of O₂F₂ was then condensed on the BrF₃ surface. The bath temperature was slowly raised and at about 130°K, the reaction between BrF₃ and O₂F₂ began, forming a violet-brown compound, with some gas evolution. Analysis showed that the gas evolved consisted mainly of oxygen (with a small amount of fluorine), which forms according to the reaction:

\[ \text{BrF}_3 \cdot \text{O}_2\text{F}_2 \rightarrow \text{BrF}_5 + \text{O}_2 \]

The colorless liquid reaction product was identified as BrF₅. The small amount of F₂ gas formed is due to partial decomposition of O₂F₂.

The yield of the violet-brown compound was about 80%. The compound began to decompose at 150°K. and decomposed completely at 170°K. to oxygen and BrF₅.

B. The O₂F₂ + SF₄ Reaction

The sulfur analog of ClF, sulfur tetrafluoride, SF₄, can also form an intensely violet-colored compound. The difficultly reproducible reaction proceeds most likely in accordance with the equation:

\[ \text{O}_2\text{F}_2 + \text{SF}_4 \rightarrow \text{O}_2\text{SF}_6 \].
Pure $\text{O}_2\text{F}_2$ and $\text{SF}_4$ react violently in accordance with the equation:

$$\text{O}_2\text{F}_2 + \text{SF}_4 \rightarrow \text{SF}_6 + \text{O}_2 \quad -121.5 \text{ Kcal}.$$ 

without the formation of an intermediate violet product. In an attempt to prevent a violent reaction both reactants were diluted with perchloryl fluoride. This solvent was used earlier in the $\text{O}_2\text{F}_2 + \text{ClIF}$ reaction.

The solubility of sulfur hexafluoride, $\text{SF}_6$, in $\text{ClO}_3\text{F}$ at low temperatures was found to be much higher than the solubility of $\text{ClIF}_3$, see Fig. 2. Therefore, the separation of an intermediate product would be comparatively easy.

It was found, however, that if both $\text{O}_2\text{F}_2$ and $\text{SF}_4$ are diluted with perchloryl fluoride, the intermediate violet product either forms only in very small amounts or does not form at all.

A 12.8 wt.% $\text{O}_2\text{F}_2$ solution was used, for example. It was frozen at $90^\circ\text{K}$. and a gaseous $\text{SF}_4$-$\text{ClO}_3\text{F}$ (1:1) mixture was added in small portions containing 20-100 mg. of $\text{SF}_4$. After the addition of each portion, the reaction vessel was warmed to $130^\circ\text{K}$.

Only traces of violet compound formed, which deposited on the walls of the reaction vessel above the $\text{O}_2\text{F}_2$-$\text{ClO}_3\text{F}$ mixture. The formation of the violet compound took place only at temperature of $90^\circ-116^\circ\text{K}$. At $130^\circ\text{K}$. a slow visible reaction between $\text{O}_2\text{F}_2$ and $\text{SF}_4$ began with evolution of $\text{O}_2$ gas and formation of $\text{SF}_6$. 
Figure 1.

Solvate of SF$_6$ and ClF$_3$ in CO$_2$. 
Further warming to 150°-170°K. increased the reaction rate and caused decomposition of the violet compound. Also decomposition of O$_2$F$_2$ to O$_2$ and F$_2$ was noted.

Use of a smaller amount of diluent gave a larger quantity of the violet product, but the reaction was difficult to control.

Sulfur tetrafluoride diluted with ClO$_3$F was distilled into the reaction tube containing frozen O$_2$F$_2$ at 90°K. Traces of a violet-purple compound formed immediately on the walls of the reaction vessel, even at 90°K. Most of the SF$_4$ and ClO$_3$F condensed on the walls above the O$_2$F$_2$. The tube was then warmed above 125°K. At about 130°K. the SF$_4$-ClO$_3$F mixture began to melt and flow down to the O$_2$F$_2$. More purple-violet compound formed and the reaction went out of control with an explosively violent evolution of gas and heat. The excess O$_2$F$_2$ remained on the bottom of the shattered reaction tube.

C. Irradiation of SF$_4$ + O$_2$ with Ultraviolet Light

In contrast to ClF, sulfur tetrafluoride does not produce colored compounds with gaseous oxygen at two atmospheres pressure, when exposed to ultraviolet light. Sulfur tetrafluoride + O$_2$ was irradiated under the conditions used for ClF$_3$ + O$_2$, in the temperature range of 90°-195°K. No violet compound was formed.
VI. CHEMICAL BEHAVIOR OF O₂F₂ WITH FLUORIDES
OF ELEMENTS CLOSE TO OXYGEN AND
FLUORINE IN THE PERIODIC SYSTEM

A. The Reaction of O₂F₂ with PF₃

The phosphorus analog of ClF, namely the phosphorus tri-
fluoride, PF₃ (an analog in the same sense as BF₃, SF₄ and IF₅, i.e., in
that all these compounds add two atoms of fluorine to form the
highest fluoride of the element), does not form a colored
addition compound with O₂F₂.

Dioxygen difluoride, however, does react with PF₃ forming
oxygen and PF₅. At the same time some of the oxygen liberated
reacts with PF₃, forming a solid, white compound at 0°C. The white
compound is fairly stable at 0°C. This compound is the only solid
reaction product; it is not the well known POF₃, which melts at
233.4⁰K. and boils at 233.8⁰K. but is an interesting polymer of
POF₃. On standing at 0°C. or at room temperature, the polymer
depolymerizes completely to POF₃ (which was identified by its
infrared spectrum) according to the equation:

\[(POF₃)ₙ \rightarrow n(O = \overset{F}{P} \overset{F}{P})\].

Gaseous PF₃ was introduced in small portions (15-50mg.)
into a Pyrex glass reaction tube containing O₂F₂ frozen at 90⁰K. The
PF₃ solidified on the walls above the O₂F₂. The tube was then
warmed slowly to 125⁰K. Both O₂F₂ and PF₃ melted and reacted at
this temperature with gas evolution to form a white solid. If the amount of PF$_3$ added in one portion was larger than 50 mg. or if the compounds were warmed quickly, the reaction proceeded with flame. The gas evolved was found to be oxygen. Phosphorus pentafluoride and polymeric POF$_3$ were identified as the reaction products:

\[
\begin{align*}
O_2F_2 + PF_3 & \rightarrow PF_5 + O_2 \\
O_2F_2 + 3 \text{PF}_3 & \rightarrow PF_5 + 2 \text{(POF}_3)_n
\end{align*}
\]

B. The Reaction of O$_2$F$_2$ with IF$_5$

In contrast to BrF$_3$, the analogous iodine compound, IF$_5$, does not form a colored compound. It was found that O$_2$F$_2$ decomposes in the presence of IF$_5$ to O$_2$ and F$_2$, without the formation of IF$_7$. Under the same conditions both ClF and BrF$_3$ formed violet addition compounds.

Liquid IF$_5$ was distributed on the walls of a reaction vessel and frozen at 90$^\circ$K. The equivalent amount of O$_2$F$_2$ was then condensed upon the IF$_5$ surface. The reaction vessel was then warmed slowly to 195$^\circ$K. There was no reaction between O$_2$F$_2$ and IF$_5$ over the temperature range 90$^\circ$-195$^\circ$K. Only a slow decomposition of O$_2$F$_2$ to O$_2$ and F$_2$ occurred.

C. The Reactions of O$_2$F$_2$ with SiF$_4$ and CF$_4$

Solid SiF$_4$ (m.p. 183$^\circ$K.) does not react with liquid O$_2$F$_2$. 
Approximately 20% SiF₄ is soluble in liquid O₂F₂ at 150°C without noticeable formation of addition compounds. At about 195°C, O₂F₂ decomposes into O₂ and F₂, while SiF₄ remains unchanged.

A measured amount of SiF₄ was added to a known amount of O₂F₂ cooled in a reaction vessel to 90°C. The O₂F₂:SiF₄ molar ratio was 1:0.4. The reaction vessel was warmed to 120°C. The O₂F₂ melted and dissolved some SiF₄, but did not react. The temperature of the bath was then increased to 150°C. More SiF₄ dissolved but no reaction occurred. After 2 hrs. at 150°C, the reagents were separated by distillation. Silicon tetrafluoride was collected in a U-tube and its purity was checked by infra-red spectroscopy and by melting point and vapor pressure measurements. O₂F₂ was decomposed to O₂ and F₂ which were identified by standard procedures.

Similarly, carbon tetrafluoride, CF₄, does not react with O₂F₂.

D. The Reaction of O₂F₂ with N₂F₄

Dioxygen difluoride does not react with NF₃ but does react with the lower fluoride of nitrogen, tetrafluorohydrazine, N₂F₄.

According to Johnson and Colburn⁸ condensation of cold

gaseous \( \text{N}_2\text{F}_4 \) (-30°C.) at relatively high pressures, gives a water-white liquid. However, if the gas is condensed at elevated temperatures and low pressures, the liquid obtained has color varying from light blue to blue-black. The intensity of color is said to be a function of the concentration of NF\(_2\) radicals in the gas phase prior to condensation and is supposedly due to an "association compound."

Our experience with \( \text{N}_2\text{F}_4 \) showed that upon distillation, either in Pyrex glass or in a Kel-F system, a violet compound is formed; it looks like the violet compound formed by the reaction between \( \text{O}_2\text{F}_2 \) and ClF but it has different properties.

A series of experiments was performed to determine the nature of this compound before using \( \text{N}_2\text{F}_4 \) for the reaction with \( \text{O}_2\text{F}_2 \). It was made clear that this violet compound is not of the same type as was obtained in the \( \text{O}_2\text{F}_2 + \text{ClF} \) reaction.

The violet compound formed by \( \text{N}_2\text{F}_4 \) can be distilled from one vessel into another together with \( \text{N}_2\text{F}_4 \) without decomposition, whereas our violet compound is nonvolatile.

About 0.6 g. \( \text{O}_2\text{F}_2 \) was reacted in a Kel-F system with 1.4 g. \( \text{N}_2\text{F}_4 \) at 130-170\(^\circ\text{K}\). A visible reaction started at 170\(^{\circ}\text{K}\) without the formation of any colored compounds.

The reaction products were \( \text{O}_2 \) and \( \text{NF}_3 \). The \( \text{O}_2 \) was
identified by pyrogallol absorption and NF₃ as a colorless liquid in liquid N₂ (b.p. = 77°C), while the original N₂F₄ is a white solid with a melting point of 110°C.

The most probable reaction is:

\[ \text{O}_2\text{F}_2 + \text{N}_2\text{F}_4 \rightarrow \text{O}_2 + 2 \text{NF}_3. \]
VII. EXPERIMENTS IN A U-SHAPE ELECTRICAL-DISCHARGE TUBE

The preparation of $O_2F_2$, $O_3F_2$ and $O_4F_2$ by an electrical-discharge method is best performed in specially designed vessels.* Entirely different reaction products may form in reaction vessels of different sizes and shapes.

An electrical discharge was passed, for example, through a $1.50_2F_2$ gas mixture (adequate for the preparation of $O_3F_2$) in the U-shape electrical discharge tube shown in Fig. 3. The conditions were: $T = 77$ K., $P = 12-17$ mm. Hg., $V = 2000-2500$ v., $A = 20-30$ ma. Under these conditions $O_3F_2$ forms in the vessel recommended. But in the U-shape vessel, three quite different products were obtained: ozone, dioxygen difluoride and traces of a violet compound not yet investigated. The wall of the left side of the U-tube (the part where the $O_2-F_2$ mixture enters) was covered with a deposit of $O_2F_2$. On the wall of the lower part of the right side a blue layer of ozone was formed, while on the wall of the upper part of the right side (above the ozone ring) a very small amount of a violet compound was deposited. Several mild explosions occurred in the gaseous phase during the operation owing, most probably, to the formation of ozone. This was never the case in the recommended type of reaction vessel.

(*) See Fig. A-2 and A-3 in the Appendix of this Report.
Figure 5.
The U-shaped discharge tube

- **O.D. = 28 mm**
- **Length of Discharge = 13 cm**
- **O.D. = 18 mm**

**LEVEL OF LIQUID N₂**

11/2 O₂ + F₂ Mix
It is known that at temperatures above $125^\circ K.$, liquid ozone causes explosions with liquid $O_2F_2$. We avoided, therefore, mixing these compounds.

The traces of the unknown violet compound resemble the violet compound obtained from the $O_2F_2 + ClF$ reaction or from the reaction between $O_2$ and $ClF_3$ under ultraviolet light. If the formation of this violet product is due to the presence of traces of chlorine-containing compounds, its nature would be the same as that of our violet product obtained in the $O_2F_2 + ClF$ reaction. To investigate this possibility, experiments were performed with $O_2 + F_2 + ClF$ mixtures.

Attempts were made to synthesize the violet compound directly from a gaseous mixture of $O_2 + F_2 + ClF$, by passing an electrical discharge. A U-shape reaction tube, shown in Fig. 3 was used. To avoid a possible explosion if the reaction

$$ClF + F_2 \rightarrow ClF_3 - 26.5 \text{ Kcal.}$$

took place, only 3.3 vol.% $ClF$ was added to the 1:1 oxygen-fluorine mixture. The gaseous $O_2 + F_2 + ClF$ mixture was fed into the reaction vessel cooled in a liquid oxygen or liquid nitrogen bath. There was no difference in the results obtained at 90° and 77°K. An electrical discharge of 15-25 mA, 2000-3000V., was sent through the mixture at a pressure of $12 \pm 5 \text{ mm Hg}$.

Dioxygen difluoride and some trioxygen difluoride were formed as a precipitate on the walls of the cooled part of the U-tube between the electrodes. In addition, a grey-blue deposit (most probably ozone) appeared on the walls of the inlet side of the tube above the electrode. Some unreacted ClF also deposited just above the grey-blue compound. However, no violet compound was formed.

When the temperature was increased to 1200K., the grey-blue deposit disappeared. The melted ClF flowed down and combined with the O₂F₂ to form the violet compound (as in the usual O₂F₂ + ClF reaction), and ClF₃.
VIII. REMARKS ON HYDROGEN SUPEROXIDE, $\text{H}_2\text{O}_4$

In the First Annual Progress Report for the Office of Naval Research, 1960, (pp. 34-43), the synthesis and the characteristics of hydrogen superoxide, $\text{H}_2\text{O}_4$, were described. Hydrogen superoxide was produced by the bombardment of $\text{O}_3$ with hydrogen atoms at 770K. The product obtained by us contained 52 wt.% of $\text{H}_2\text{O}_4$.

It is of interest that Zaslowsky, Martinez and Wojtowicz\(^{10}\) of the Olin Mathieson Chemical Corporation have recently confirmed our findings and substantially increased the yield of $\text{H}_2\text{O}_4$. In nearly all their experiments, the molar ratio of oxygen to hydrogen peroxide is 1:1. This fact strongly supports the existence of a stoichiometric compound. The highest concentration obtained was 72 wt.% $\text{H}_2\text{O}_4$ and 28 wt.% $\text{H}_2\text{O}$. Regardless of the interpretation the important fact is that substantial quantities of oxygen above the composition $\text{H}_2\text{O}_2$ are introduced into the solid.

The above-named authors made the following statement:

"No explanation can be offered at the present time to account for the failure by Giguere and Chin\(^{11}\) to detect the superoxide by the spectroscopic method."


As we pointed out previously Giguere and Chin did not analyze their product for surplus oxygen content. Thus, it is not certain that they actually prepared $\text{H}_2\text{O}_4$.

Nekrasov, Skorohodov and Kobozev have emphasized$^{12}$ that Giguere and Chin$^{11}$ used solid, rather than liquid, $\text{O}_3$. In the opinion of the Soviet investigators, Giguere and Chin did not preclude the stabilization of the $\text{HO}_2$ radical by diffusion into the liquid $\text{O}_3$, but on the contrary increased its reduction by atomic hydrogen to $\text{H}_2\text{O}_2$.

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APPENDIX
THE REAGENTS USED

Dioxygen difluoride, $O_2F_2$, was prepared directly from the elements, essentially by the method described by Ruff and Menzel\(^1\) and by Aoyama and Sakuraba.\(^2\) The flow diagram for our modified apparatus is shown in Fig. A-1. The 1:1 gaseous mixture of fluorine and oxygen is prepared in the perfluorinated stainless-steel cylinder. The cylinder has a volume of about 8 l. and is used at pressures up to 80 p.s.i.a. The $O_2$-$F_2$ mixture is fed from this cylinder through the flowmeter containing Kel-F oil, through the trap cooled with liquid oxygen to eliminate impurities condensable at this temperature and into the reaction vessel. The reaction vessel 6.5 cm. in diameter and 18 cm. long, is made of Pyrex glass; it is cooled to 77 or 90°K. A detailed sketch of the reaction vessel is shown in Fig. A-2.

A high-voltage electrical discharge is established in the reaction vessel between two copper electrodes, which are fixed 10-cm. apart. The electrodes are 2 cm. in diameter and are connected to copper wires sealed into the reaction vessel by Teflon plugs. The other plugs in the system have ground-glass joints that are

\(^{(1)}\) Ruff, O., and Menzel, W., Z. anorg. allgem. Chem., 211, 204 (1933).

FIGURE A-21.

REACTION VESSEL FOR PREPARATION OF OF
lubricated with Kel-F grease. The discharge varies from 25 to 30 ma. at 2100-2400V. The flow of the F\textsubscript{2}-O\textsubscript{2} mixture is adjustable so that the pressure in the reaction vessel is maintained at 12 ± 5 mm. Hg.

The electrical part of the apparatus consists of a 110-5000V, 60-cycle, single-phase transformer, in series with a 1000-ohm Ohmite vitreous enameled limiting resistor, together with a 0-100 milliammeter and a 0-5000 voltmeter.

The formation of dioxygen difluoride consumes all the entering F\textsubscript{2}-O\textsubscript{2} mixture. The product condenses in solid form on the walls of the reaction vessel. When the preparation is completed, the electrical discharge and the gas supply are stopped, the reaction vessel is warmed to dry-ice temperature and the O\textsubscript{2}F\textsubscript{2} is distilled into the storage cylinder cooled in a liquid-nitrogen bath. Distillation is conducted at reduced pressure; all the connecting tubes must be cooled with dry ice. Some O\textsubscript{2}F\textsubscript{2} may decompose upon distillation. Therefore, the O\textsubscript{2} and F\textsubscript{2} formed must be pumped off while the O\textsubscript{2}F\textsubscript{2} is cooled with liquid nitrogen.

Sodium fluoride, NaF pellets (ignited) are placed into the reaction and storage vessels, in order to remove any HF and SiF\textsubscript{4} which may have formed. NaF combines with these compounds according to the equations:
\[ \text{NaF} + \text{HF} \rightarrow \text{NaF} \cdot \text{HF} \]
\[ 2\text{NaF} + \text{SiF}_4 \rightarrow \text{Na}_2\text{SiF}_6 \]

Pure dioxygen difluoride can be stored for extended periods of time in Pyrex glass cylinders cooled to 900K.

Trioxygen difluoride, \( \text{O}_3\text{F}_2 \), was prepared by a method similar to that used for preparing \( \text{O}_2\text{F}_2 \). The gaseous \( \text{F}_2-\text{O}_2 \) mixture must contain three volumes of \( \text{O}_2 \) and two volumes of \( \text{F}_2 \). This mixture is found to combine quantitatively to form \( \text{O}_3\text{F}_2 \) in the same type of apparatus that is used for \( \text{O}_2\text{F}_2 \) preparation.\(^3\),\(^4\),\(^5\) The construction of the reaction vessel is slightly different, as is shown in Fig. A-3. Slightly different also are the reaction conditions: the reaction vessel is cooled in a liquid-nitrogen bath, and the electrical discharge varies from 20 to 35 ma. at 2000-2200V. The gas pressure in the reaction vessel is the same, i.e., 12 ± 5 mm. Hg.

When the preparation is completed, the gas flow and the discharge are stopped and the reaction vessel is warmed to 900K. by changing to a liquid-oxygen bath. Trioxygen difluoride liquefies

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FIGURE A-5.

REACTION VESSEL FOR PREPARATION OF O₃F₂
and flows into the side tube. This tube is then disconnected and can be used as the storage vessel. Pure trioxygen difluoride can be stored for a long time at 770K in Pyrex-glass vessels. The rate of decomposition at this temperature is about 3.6 x 10^{-5}/hr.

Chlorine monofluoride, ClF, was prepared in our laboratories from gaseous Cl₂ and F₂ in accordance with the reaction:

\[ \text{Cl}_2 + \text{F}_2 \rightarrow 2 \text{ClF} \]

About 250 cm³/min. of each gaseous Cl₂ and F₂ were passed through a stainless-steel tube, vol. 56 cm³, at 400-500°C. The residence time was about 7 sec. The product was passed through a trap cooled with dry ice to remove ClF₃, if formed in small amounts, or excess of free Cl₂, if present, and into a second trap cooled with liquid oxygen, where ClF was condensed. The apparatus was made of Kel-F traps, stainless-steel valves and copper tubing. The product was purified by distillation and contained over 99% ClF.

Silicon tetrafluoride, SiF₄, was prepared according to the reactions:


2 CaF$_2$ + 2 H$_2$SO$_4$ $\rightarrow$ 2 CaSO$_4$ + 4 HF,

4 HF + SiO$_2$ $\rightarrow$ SiF$_4$ + 2 H$_2$O $^{7,8,9}$

The mixture of CaF$_2$, SiO$_2$ and H$_2$SO$_4$ was warmed slightly in a glass flask, and the gas formed was passed through two traps cooled with dry ice (to separate the possible excess of HF) into a glass trap cooled with liquid O$_2$, where SiF$_4$ was condensed. The product was purified by sublimation.

Phosphorus trifluoride, PF$_3$, was prepared according to the reaction:

$$PCl_3 + 3 HF \rightarrow PF_3 + 3 HCl.$$ $^7$

Nitryl fluoride, NO$_2$F, was prepared in our laboratories according to the equation:

$$2 NO_2 + F_2 \rightarrow 2 NO_2F.$$ $^7$

All other reagents were the commercial products of the highest available purity as supplied by Stauffer Chemical Co., General Chemical Division of Allied Chemical Co., Pennsalt Chemicals Corp., E. I. du Pont de Nemours and Co., Matheson Co., Air Reduction Co. and others.

Most of these reagents were further purified by fractional distillation.

\[\text{(8) Lebouche, L., Fischer, W., and Biltz, W., Z. anorg. allgem. Chem., 207, 64 (1932).}\]

\[\text{(9) Ruff, O., and Ascher, E., Z. anorg. allgem. Chem., 196, 413 (1931).}\]