SAFE HANDLING OF CHLORINE TRIFLUORIDE
AND THE CHEMISTRY OF THE
CHLORINE OXIDES AND OXYFLUORIDES

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SAFE HANDLING OF CHLORINE TRIFLUORIDE AND THE CHEMISTRY OF THE CHLORINE OXIDES AND OXYFLUORIDES

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A discussion of the potential hazards of chlorine trifluoride is presented and a series of safe handling procedures is recommended. Particular emphasis is placed on the hazardous chlorine oxides and oxyfluorides which are produced by reaction of chlorine trifluoride with moisture and many oxides. Modification of the procedures for use with bromine trifluoride is included. The report contains a comprehensive literature survey on the preparation, chemical and physical properties, and stability of the individual chlorine oxides and oxyfluorides.
# Safe Handling of Chlorine Trifluoride and the Chemistry of the Chlorine Oxides and Oxyfluorides

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SAFE HANDLING OF CHLORINE TRIFLUORIDE AND THE CHEMISTRY OF THE CHLORINE OXIDES AND OXYFLUORIDES

Chlorine trifluoride is an extremely useful chemical in many operations requiring a high energy fluorinating agent. However, those factors which make it useful also contribute to a handling hazard with the compound. One of these hazards, which has received relatively little attention in the past, is the ease of formation of chlorine oxides when moisture or certain oxides come into contact with the compound. It is for this reason that this report is prepared. A literature survey on the preparation and stability of the chlorine oxides and oxyfluorides is included so that one can see the interrelation of these compounds and know something of their hazardous nature. Since it is not known with which of these compounds one is dealing, it was necessary to include information on all the chlorine oxides and oxyfluorides which are known to exist. It is hoped that this report will provide for safer handling of the compound through a better understanding of the chemistry involved.

POTENTIAL HAZARDS OF CHLORINE TRIFLUORIDE

The potential hazards associated with the use of chlorine trifluoride are twofold. 1) It is an extremely vigorous fluorinating agent and is therefore unstable in the presence of easily fluorinated material. 2) It reacts with limited amounts of water and with many chemical trapping agents to produce chlorine oxides which are themselves very unstable materials.

Table I lists calculated values for the heats of reaction of several materials to illustrate the magnitude of the heats of fluorination. The largest value is for the reaction with a typical hydrocarbon, n-hexane. For comparison, the heat of combustion of n-hexane is \(-921\) kcal./mole; thus, it is apparent that a large amount of heat is liberated rapidly in a reaction of this type. When uncontrolled amounts of chlorine trifluoride are inadvertently mixed with compounds containing carbon and hydrogen, an explosion almost always results, initiated by the very large heat of reaction. Common materials of this type are ordinary pump oils, cork, paper, rubber, etc.

**TABLE I**

**CALCULATED HEATS OF REACTION AT 25°C.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heat of Reaction (kcal./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cl}_3F(g) + \text{Ni(s)} \rightarrow \text{NiF}_2(s) + \text{ClF}(g))</td>
<td>-134</td>
</tr>
<tr>
<td>With nickel</td>
<td></td>
</tr>
<tr>
<td>(19 \text{Cl}_3F(g) + \text{C}<em>6\text{H}</em>{14}(l) \rightarrow 19 \text{ClF}(g) + \frac{1}{2} \text{HF}(g) + 6 \text{CF}_4(g))</td>
<td>-1730</td>
</tr>
<tr>
<td>With n-hexane</td>
<td></td>
</tr>
<tr>
<td>(\text{Cl}_3F(g) + \text{C}_2\text{HCl}_3(l) \rightarrow 2 \text{CF}_3\text{Cl}(g) + \frac{1}{2} \text{HF}(g) + 5 \text{ClF}(g))</td>
<td>-325</td>
</tr>
<tr>
<td>With trichloroethylene</td>
<td></td>
</tr>
<tr>
<td>*n-hex, normal hexane; TCE, trichloroethylene.</td>
<td></td>
</tr>
</tbody>
</table>
Table I also indicates that the heat of reaction with nickel is a rather large value though not as high as with organic compounds. Nickel is generally conceded to be a very good material of construction for use with chlorine trifluoride even though the two materials are potentially capable of vigorous reaction. Nickel fluoride, the product of this reaction, adheres well to the surface of the nickel metal, and even very thin films of this reaction product are an effective barrier to reaction between the two materials. This barrier limits the availability of one or both of the reactants so that the reaction is slowed to a velocity which is governed by the diffusion rate of one of the materials through this barrier film. Also the thin film has good thermal contact with the bulk nickel so that the heat of reaction is quickly dissipated to the metal, preventing a large temperature rise.

One can obtain conditions, however, as with finely divided metals, when this heat is not readily dissipated; and under such conditions, the temperature of the thin film of product fluoride increases. As the temperature increases, the reaction rate or the diffusion rate of reactant material increases, thus liberating heat at an ever increasing rate. If the quantity of chlorine trifluoride available to this reacting surface is not limited, an explosion can result.

The reactions with organic compounds or finely divided metals might occur in new or modified equipment or on surfaces which have not been previously exposed to fluorine or chlorine trifluoride. The other source of hazard with chlorine trifluoride handling is the production of chlorine oxides - very unstable materials - which result from reaction with water, soda-lime, or oxides. The hazard is greatest when water and chlorine trifluoride are in approximately equal mole ratio. Chlorine oxides are known to be formed by reaction of chlorine trifluoride and water, although it is impossible to write an exact equation for the process at this time. It appears quite likely that the products, the particular chlorine oxides, vary depending on the degree of excess of either of the two reagents. All possible chlorine oxides may be encountered from this reaction; at least none can be ruled out at this writing.

It should be remembered that water is always present in equipment which has been opened to the atmosphere, especially if sufficient time has been allowed for adsorption equilibrium with atmospheric moisture. The total amount of moisture adsorbed on a piece of equipment will depend upon the absolute or real surface area of the equipment. This real surface area is usually much larger than the geometric surface area because of microscopic roughness. One monolayer of water contains about 0.3 mg. of water per square meter of real surface. At relative humidities of 40% or more, one can expect adsorption in excess of monolayer adsorption. Much larger quantities of water will be present if there are compounds which take up water of hydration, such as copper fluorides, iron fluorides, or uranyl fluoride, to name a few. In these reactions, where chlorine oxides are formed, the chlorine trifluoride is in slight excess or approximately equal mole ratio.
In a situation involving adsorbed water or water of hydration, the greatest hazard is not necessarily the contact of the chlorine trifluoride with the wet surface, because the chlorine oxides when formed are usually in low concentration. The hazard comes in some later operation involving cold trapping where the undesirable compound is condensed, and the concentration may reach the hazardous level.

Chlorine oxides are known products of the reaction of chlorine trifluoride and soda lime, a common chemical trapping agent. It is not known whether the origin of the compound is the reaction with the soda lime (a mixture of sodium and calcium oxides and hydroxides) or with the water which is nearly always present in such a system. Again any cold trapping operation downstream from the soda lime trap may concentrate all the chlorine oxides. Preliminary observations have indicated that a chemical trap operated at elevated temperatures (100°C. or higher) will generate less chlorine oxides than one operated at a lower temperature.

Any uncontrolled, large release of chlorine trifluoride, whether liquid or vapor, will probably result in fires, burning any material nearby. While water and chlorine trifluoride are a potentially hazardous mixture, one should recognize that, in the event of a major release of the chemical, water in very great excess constitutes the most satisfactory method of combating the emergency. When life or extensive property are endangered, use of copious amounts of water serves to extinguish the resulting fires, destroy any unreacted chlorine trifluoride, and dilute any chlorine oxides to harmless concentrations.

RECOMMENDED SAFE HANDLING PROCEDURE

The potential hazards of chlorine trifluoride have just been discussed in the preceding section, and the recommended safe handling procedures are designed to minimize these two hazards accompanying use of the compound. The procedures are largely designed for use of chlorine trifluoride in the vapor phase, but many are applicable for use also in the liquid phase. These procedures have been drawn up through operating experience, by application of the best knowledge available on the chemistry of the system, and last but not least, by the application of common sense to a hazardous situation.

General

1. In any reaction, use the minimum amount of chlorine trifluoride which will adequately and satisfactorily accomplish the job.

2. The source of chlorine trifluoride should have both "cut-off" and "throttling" valves so that in the event of an unexpectedly rapid or violent reaction, the source can be valved off and thus prevent uncontrolled propagation. One should never throttle a flow of chlorine trifluoride with the cylinder or container valve.

3. Before chlorine trifluoride enters a system, especially a new or recently altered system, one should ascertain that no hydrocarbons,
oils, greases, or other foreign materials are present in the equipment, especially in dead-end sections of the equipment. It is well to pretreat a new or altered system with fluorine if available or dilute chlorine trifluoride before introducing pure chlorine trifluoride. When the first introduction of chlorine trifluoride is made, this introduction should be made slowly so that if the unexpected does occur, one can quickly stop the input of reactant gas.

4. Contact or reaction of chlorine trifluoride with water, moist surfaces, or reactive oxides will almost always be accompanied by production of chlorine oxides; therefore, one should ascertain beforehand that adequate provisions have been taken to prevent uncontrolled and explosive reactions. (See top of page 17.)

5. If production of chlorine oxides cannot be prevented, be sure that their concentration or pressure is maintained low. Avoid condensation or concentration of even small amounts of these compounds. Adequate precautions involve use of suitable shields or barriers to isolate the equipment where these compounds might be encountered. (See item 2, page 8.)

6. Avoid contact of chlorine trifluoride with any material not previously known to be satisfactory; or if contact is necessary, use extreme care.

7. Recognize that in the event of a leak or uncontrolled release of chlorine trifluoride, this chemical can react with materials in the immediate vicinity. If the release is of sufficient magnitude, fires will almost certainly ensue. Observe good housekeeping in general so that personnel can be evacuated quickly in an emergency.

8. Use of liquid chlorine trifluoride is usually more hazardous than vapor phase reactions since more moles of fluorinating agent are present per unit area of reactant surfaces. There are cases, however, where the vapor phase is more hazardous because heat transfer and heat removal are poorer from the reactant surface allowing, under extreme conditions, an uncontrolled heat rise. Use of the first three rules above should minimize this hazard.

Personal Precautions

1. Avoid contact of chlorine trifluoride with the skin and especially the eyes. Wear clean gloves of neoprene or polyvinyl chloride material and a Fluorothane face shield when this type of contact is a possibility. Safety glasses should be worn at all times when handling chlorine trifluoride.

2. Avoid inhaling the vapor; provide sufficient ventilation.

3. The U. S. Army combat gas mask equipped with the M11 cannister may be relied on in areas of low concentration. For emergency use, impermeable polyvinyl chloride suits which completely enclose the wearer with a self-contained or piped air supply are recommended. However, no personnel protective devices are available for use in areas of high
concentration of the vapor.

4. First aid in the event of personal contact requires a) removal from contaminated atmosphere, b) flooding immediately with a large quantity of water such as from a safety shower until medical attention arrives.

Disposal of Chlorine Trifluoride

1. Venting to the atmosphere is probably the safest disposal technique where adequate facilities are available. The facilities involve use of a stack and strong purge streams to dilute the gas and expel it into a region where no personnel exposure can be made and where corrosion is not too severe a problem.

2. For small scale disposal operations, e.g., laboratory scale operations, a satisfactory technique involves the use of a vacuum pump preceded by a tower containing soda lime, activated alumina, or both. It is important that no cold trap be placed between the tower and the pump, since chlorine oxides will be evolved from the tower and condensed or concentrated by a cold trap. One should recognize that no readily available indicator is known for informing the operator that the absorbing capacity of the tower has been expended. The tower should be recharged at frequent intervals. Many operators prefer that the pump be filled with a fluorocarbon lubricating oil which will allow trace amounts of chlorine trifluoride to pass through the pump as the end of the trap life is approached. As the chemical trap capacity nears exhaustion, trace amounts of chlorine trifluoride appear in the pump discharge. Detection of the noxious odor of this material indicates the need for recharging the trap.

Another school of thought advocates use of a hydrocarbon lubricating oil in the pump. Again the tower should be recharged at frequent intervals. If, however, small amounts of chlorine trifluoride do pass the trap, they are in low concentration and slowly build up a sludge in the pump oil. Only a small amount of sludge is required to freeze-up the pump thus stopping the flow of low concentration chlorine trifluoride. In this manner it is readily apparent that the tower is expended. A good washing of the pump with a degreasing agent, such as trichloroethylene, followed by fresh oil will usually restore the vacuum pump to satisfactory operation.

Emergency Situations

1. Defective containers of chlorine trifluoride (defective valves, cracked cylinders, etc.) should be frozen down with dry ice and transported immediately out of the work area. Disposal is best made into a holding pond or protected body of water where the container can be punctured and the contents safely reacted with a large excess of water. Small containers (less than 1/2 lb.) can be taken in the frozen condition to an isolated, rocky or barren area of 1 acre or more where they may be allowed to warm up, expelling the vapor to the atmosphere.
2. At normal pressures and temperatures, large uncontrolled releases of gaseous fluorinating agents may be safely controlled by use of water fog applied by hose streams. Personnel assigned should be provided with complete body and respiratory protection as provided by polyvinyl chloride, air-supplied suits. See section on personal protection.

3. Releases of large amounts of liquid chlorine trifluoride will produce violent reactions resulting in fire. Small amounts of water may tend to cause the fire to spread. However, the use of copious quantities of water may be warranted, as a lesser risk, if life or extensive property is endangered.

**Modification of the Above Procedure when Bromine Trifluoride is Employed**

Bromine trifluoride is essentially as reactive, from the safety standpoint, as chlorine trifluoride. It does not, however, produce a series of explosive oxides comparable to the chlorine oxides. From this viewpoint, it is less hazardous than chlorine trifluoride. On the other hand, it also is a powerful fluorinating agent with a much lower volatility than chlorine trifluoride. Its greatest hazard arises, therefore, from its being inadvertently condensed, thus being retained where some later operation may introduce an easily oxidized material. The following rules are applicable for bromine trifluoride.

**General and Personal**

1. All the general and personal rules which have been stated for chlorine trifluoride are equally applicable for bromine trifluoride with the exception of those dealing with the explosive chlorine oxides.

2. All lines through which bromine trifluoride vapor is passed should be adequately heated to prevent condensation of liquid bromine trifluoride.

**Disposal of Bromine Trifluoride**

1. Disposal of bromine trifluoride from small-scale operations may be accomplished by use of a soda lime or activated alumina tower which is heated to prevent contact by liquid bromine trifluoride. A cold trap is recommended between the tower and the pump if a fluorocarbon oil is employed in the pump. Otherwise, small amounts of bromine trifluoride would dissolve in the oil as the tower approached the end of its useful life. The hazard comes in not knowing that bromine trifluoride exists in the pump and later using the equipment under conditions where an easily oxidizable material is brought into contact with the bromine trifluoride in the pump oil.

2. Disposal of large quantities of bromine trifluoride should be handled in the same manner as for chlorine trifluoride.
Miscellaneous

1. Commercial shipment of these very reactive fluorinating agents is permitted only in cylinders prescribed by the Interstate Commerce Commission.

2. Cylinders containing these materials should be identified both by label and color code as to their contents.

3. During storage, cylinders containing these chemicals should be chained or adequately supported and, insofar as practicable, isolated from combustible material.

THE CHEMISTRY OF THE CHLORINE OXIDES AND OXYFLUORIDES

While chlorine gas will not combine with oxygen directly, four binary compounds of these elements are known. In the order of increasing oxidation state of the chlorine atom these compounds are: chlorine monoxide, Cl₂O; chlorine dioxide, ClO₂; chlorine trioxide or hexoxide, a monomeric-dimeric pair, 2ClO₃ ↔ Cl₂O₆; and chlorine heptoxide, Cl₂O₇. In addition to these compounds, others have been mentioned from time to time. The compound ClO has never been isolated, but kinetic studies on the thermal and photochemical decomposition of the monoxide and dioxide appear to require its existence. It is apparently extremely unstable and decomposes to chlorine and oxygen or combines with other chlorine oxides. The compound Cl₂O₂, while mentioned in the early literature (24), is now known not to exist as such, except perhaps as a short lived intermediate in thermal decomposition of higher oxides. The last binary compound is chlorine tetroxide, ClO₄, first reported in 1923 (15) and later postulated as an intermediate in the fluorination of perchloric acid (14). The evidence for the existence of this compound is not conclusive, and several authors have explained the earlier results without resort to the hypothetical tetroxide. It does appear to be a short lived intermediate at certain temperatures.

In the detailed discussion of the chemistry of the four known chlorine oxides, use has been made of several excellent reviews of these compounds; namely, Sidgwick, Chemical Elements and Their Compounds (36) and Supplement II to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry (22). The oxyfluorides of chlorine are compounds whose properties have been studied much more recently. At the present time there are three known compounds, chloryl fluoride, ClO₂F; perchloryl fluoride, ClO₃F; and fluorine perchlorate, FCIO₄. Upon hydrolysis of chlorine trifluoride, a red liquid thought to be ClOF was reported by Ruff (30), but nothing further is known about this compound.

The physical and chemical properties of the chlorine oxides and oxyfluorides are presented in table II along with those of chlorine and fluorine included for comparison. A detailed discussion of the chemistry of these compounds is presented in the following pages. In the case of all the chlorine oxides, they cannot be prepared by direct union of the elements.
<table>
<thead>
<tr>
<th>Formula</th>
<th>Chlorine</th>
<th>Chlorine Monoxide</th>
<th>Chlorine Dioxide</th>
<th>Chlorine Trioxide</th>
<th>Chlorine Heptoxide</th>
<th>Chlorine Fluoride</th>
<th>Perchloro Fluoride</th>
<th>Fluorine Peroxide</th>
<th>Fluorine</th>
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<td>Melting Point, °C.</td>
<td>Cl₂</td>
<td>Cl₂O</td>
<td>Cl₂O₃</td>
<td>Cl₂O₅</td>
<td>Cl₂O₁₇</td>
<td>Cl₂O₉</td>
<td>Cl₂OF</td>
<td>Cl₂OF</td>
<td>F₂</td>
</tr>
<tr>
<td></td>
<td>108</td>
<td>116</td>
<td>59</td>
<td>5.5</td>
<td>515</td>
<td>115</td>
<td>1.46 ± 0.2</td>
<td>0.00</td>
<td>92.3</td>
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<td>Boiling Point, °C.</td>
<td>33.7</td>
<td>2</td>
<td>11</td>
<td>200°C (max.)</td>
<td>550</td>
<td>950</td>
<td>1137 ± 2°C</td>
<td>1137 ± 2°C</td>
<td>35.0</td>
</tr>
<tr>
<td>Critical Temperature, °C.</td>
<td>144.0</td>
<td>139*</td>
<td>155</td>
<td>296*</td>
<td>296*</td>
<td>296*</td>
<td>95.17 ± 0.10</td>
<td>129</td>
<td>1138</td>
</tr>
<tr>
<td>Density at 0°C, g/cm³</td>
<td>1.64</td>
<td>1.46</td>
<td>1.06</td>
<td>1.66</td>
<td>23.0</td>
<td>102.46</td>
<td>138.56</td>
<td>92.37</td>
<td>0.44</td>
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<td>Molecular Weight</td>
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<td>84.91</td>
<td>87.46</td>
<td>150.91</td>
<td>150.91</td>
<td>150.91</td>
<td>150.91</td>
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<td>Vapor Density</td>
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<td>Normal</td>
<td>Normal</td>
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<td>Normal</td>
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<tr>
<td>Trouton Constant, e.u.</td>
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<td>23.3</td>
<td>23.3</td>
<td>23.2</td>
<td>23.2</td>
<td>23.2</td>
<td>20.4</td>
<td>20.4</td>
</tr>
<tr>
<td>2H₂O₀, form, °C/kmole</td>
<td>6.20</td>
<td>5.95</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Vapor Pressure at 0°C, mm. Hg</td>
<td>699</td>
<td>490</td>
<td>27.7</td>
<td>27.7</td>
<td>27.7</td>
<td>27.7</td>
<td>27.7</td>
<td>27.7</td>
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</tr>
<tr>
<td>2H₂O₀, form, °C/kmole</td>
<td>0.00</td>
<td>25.1**</td>
<td>24.7</td>
<td>24.7</td>
<td>24.7</td>
<td>24.7</td>
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<tr>
<td>2H₂O₀, form, °C/kmole</td>
<td>0.00</td>
<td>59.6</td>
<td>37.0</td>
<td>37.0</td>
<td>37.0</td>
<td>37.0</td>
<td>37.0</td>
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<tr>
<td>2H₂O₀, (g) kmol/s</td>
<td>8.11</td>
<td>59.6</td>
<td>37.0</td>
<td>37.0</td>
<td>37.0</td>
<td>37.0</td>
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<tr>
<td>Color and Appearance of Gas</td>
<td>yellow-green</td>
<td>brown</td>
<td>orange-yellow</td>
<td>red-brown</td>
<td>colorless, oily</td>
<td>colorless</td>
<td>colorless</td>
<td>colorless</td>
<td>colorless</td>
</tr>
<tr>
<td>Color and Appearance of Liquid</td>
<td>dark brown</td>
<td>orange-red</td>
<td>red-brown</td>
<td>as K₂Cr₂O₇</td>
<td>no direct evidence</td>
<td>yes, either gas or liquid on slightest provocation</td>
<td>yes, reacts violently with water and organics</td>
<td>yes, shock or sudden heating, but most stable chlorine oxide</td>
<td>no, but reacts violently with easily oxidized material</td>
</tr>
<tr>
<td>Explosive Structure</td>
<td>no</td>
<td>yes</td>
<td>yes, either gas or liquid on slightest provocation</td>
<td>yes, reacts violently with water and organics</td>
<td>yes, shock or sudden heating, but most stable chlorine oxide</td>
<td>no, but reacts violently with easily oxidized material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-O Distance, Å</td>
<td>1.73</td>
<td>1.33</td>
<td>1.73</td>
<td>1.73</td>
<td>1.73</td>
<td>1.73</td>
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<tr>
<td>Cl-Cl Distance, Å</td>
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<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
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<td>Cl-F Distance, Å</td>
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</table>

*By use of the 3/2 rule.
**From heat of decomposition.
Heats of formation of all these binary compounds are endothermic and all are explosive materials when present in any appreciable concentrations.

**Chlorine Monoxide**

A summary of the physical properties of this compound is presented in table II. The vapor pressure of chlorine monoxide has been measured from $-100^\circ$ to $+15^\circ$C. by Goodeve (16) and found to obey the equation

$$\log P_{mm} = 7.87 - \frac{1373}{T},$$

which has been plotted in figure 1. The temperature, $T$, is expressed in degrees Kelvin.

**Preparation.** Chlorine monoxide is the true anhydride of hypochlorous acid; thus it reacts with water according to the equation

$$\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HOC1}.$$

The monoxide has been prepared by dehydrating a hypochlorous acid solution using phosphorous pentoxide or calcium nitrate, or by passing an air stream through a hypochlorous acid solution thus vaporizing a portion of the monoxide. Since a common method of preparation of hypochlorous acid is the reaction

$$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl},$$

it is necessary to destroy the hydrogen chloride before vaporizing the chlorine monoxide.

Chlorine will react with a solid alkali metal carbonate, bicarbonate silicate, hydroxide, or phosphate to produce chlorine monoxide. This reaction has been adapted to industrial scale operation (8) at 150 to 200°C. where circulation of a charge of chlorine gas over a bed of the alkali metal compound can produce the monoxide free of chlorine contamination. This same reaction could occur in a soda lime trap used for chemically trapping chlorine trifluoride. Chlorine trifluoride reacts with soda lime, a mixture of sodium and calcium hydroxides, producing chlorine and water; the chlorine can then react with the unreacted soda lime to produce chlorine monoxide.

Other preparative reactions for the monoxide are the reaction of chlorine with mercuric oxide

$$2\text{Cl}_2 + \text{HgO} \text{ (mixed with sand to moderate)} \rightarrow \text{Cl}_2\text{O} + \text{HgCl}_2,$$

and reaction of chlorine with a potassium hypochlorite solution

$$\text{Cl}_2 + \text{KClO (aq. soln.)} \rightarrow \text{KCl} + \text{Cl}_2\text{O}.$$
VAPOR PRESSURE OF THE CHLORINE OXIDES AND OXYFLUORIDES

FIGURE 1
**Explosion Danger.** Chlorine monoxide is an explosive compound as mentioned previously. At one atmosphere total pressure and 23°C., the minimum explosive concentration (14,37) has been found to be 23 mole per cent when diluted with air or other inert gas. Up to concentrations of 30 per cent, the explosions are weak and must be initiated by sparking; but above this value, they may be violent and unpredictable. Contact of the gas with organic materials - cork, rubber stoppers, or tubing, etc. - can result in violent explosions at much lower concentrations.

At higher temperatures the explosions are more violent and the minimum explosive concentration probably is lower. The liquid frequently explodes on pouring from one vessel to another or upon boiling. The compound, therefore, is extremely hazardous.

**Photochemical Decomposition.** The photochemical and thermal decomposition of chlorine monoxide has been studied and reviewed by Schumacher (33). For this reaction, the effective light is of the same wave length as that absorbed by chlorine; namely, 4050, 4360, and 4600 A. It is also found that two molecules of the monoxide are decomposed for each quantum of light, hν, absorbed. The following mechanism has therefore been proposed by Schumacher:

1. \( \text{Cl}_2 + \text{h} \nu \rightarrow 2\text{Cl} \)
2. \( \text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{Cl}_2 + [\text{ClO}] \)
3. \( 2[\text{ClO}] \rightarrow \text{Cl}_2 + \text{O}_2 \)

for a net reaction

\( 2\text{Cl}_2\text{O} + \text{h} \nu \rightarrow 2\text{Cl}_2 + \text{O}_2 \).

**Thermal Decomposition.** The thermal decomposition of the monoxide proceeds at a measurable rate between 60° and 140°C. At the lower temperature, about 12 to 24 hours are required for complete decomposition, whereas only a few minutes are required at the higher temperature. The temperature coefficient of the reaction rate is a factor of 2.03 for each 10°C. temperature increase. Pressure changes have most commonly been used to follow the course of the decomposition reactions. An induction period is observed; then the reaction rate accelerates. After reaching a maximum, it falls to about the value obtained initially. An explosion almost invariably occurs at the end of the reaction. (See curve I of figure 2 for a plot of pressure change vs. per cent decomposition.) The reaction is a homogeneous gas reaction, being uninfluenced by the surface which is available to the gases. The velocity of the reaction in carbon tetrachloride solution is almost identical to that in the gas phase.

The time involved in the induction period is approximately inversely proportional to the initial pressure, and during this time about half of the initial chlorine monoxide is consumed. The time of the induction period can be reduced by irradiation with light and can be eliminated completely by adding a small amount of chlorine dioxide. This suggests that the dioxide or a dioxide-reaction product is involved in this induction period.
I 382.2 mm. Cl₂O At 120 °C, Beaver & Stieger (2)
II 212.1 mm. ClO₂ At 45.1 °C. In Glass Reactor A, Schumacher & Stieger (34)
III 204.7 mm. ClO₂ At 45.0 °C. In Quartz Reactor B, Schumacher & Stieger (34)
IV 208 mm. Cl₂ClO₂ (205 mm. Cl₂) At 45.1 °C. In Glass Reactor A, Schumacher & Stieger (34)

DECOMPOSITION OF CHLORINE OXIDES

FIGURE 2
The pressure increase to the maximum is accompanied by an increase in chlorine dioxide concentration as revealed by the absorption spectrum of this compound. Additions of chlorine or oxygen to the mixture do not have an effect on the reaction rate. Beyond the maximum, as the pressure decreases, the concentration of both the dioxide and the monoxide decreases, but the latter decreases more rapidly than the former. It has been assumed, therefore, that the explosion at the end of the reaction is due to chlorine dioxide, or a reaction product of this compound, and that chlorine monoxide hinders the explosive decomposition of the dioxide.

**Chlorine Dioxide**

The physical properties are outlined in table II.

**Preparation.** The usual large-scale preparation of chlorine dioxide is to bring chlorine and sodium chlorite into contact, which leads to the following reaction

\[
\text{Cl}_2 + 2\text{NaClO}_2 \rightarrow 2\text{NaCl} + 2\text{ClO}_2.
\]

This reaction may be carried out in solution or by circulating chlorine over solid sodium chlorite. Chlorine-free dioxide can be made by recycling the product stream until all the chlorine has been converted. The dioxide, as with all chlorine oxides, is extremely explosive, and explosion control of this reaction is achieved by incorporating an explosion chamber in the system and carefully regulating the pressure of the circulating gases. A small scale adaptation of this procedure has been described (20).

Another preparation is recorded, but the danger of explosion is much greater by this technique. The reaction involves a solid chlorate and sulfuric acid. Chloric acid, the intermediate which is produced, decomposes as is shown by the equation

\[
3\text{HClO}_3 \xrightarrow{\text{H}_2\text{SO}_4} 2\text{ClO}_2 + \text{HClO}_4 + \text{H}_2\text{O}.
\]

This system will detonate if rapidly heated to 100°C.

A laboratory scale procedure has been published (11) wherein 0.1 M solutions of sodium chlorite (NaClO₂) and sodium hypochlorite (NaClO) are mixed in a 2:1 ratio. To 10 to 25 ml. of this mixture is added an excess of 0.5 N sulfuric acid (about 50 ml.); and by aeration of the solution, chlorine dioxide containing 0.1% chlorine is obtained. Increasing the hypochlorite concentration serves to increase the chlorine impurity concentration.

**Explosion Danger.** Chlorine dioxide can decompose explosively on the slightest provocation either in the gaseous or liquid state. Initiation of these explosions can occur by heating, sparking, exposure to sunlight, and other processes. The following recommendations have been made for minimizing the explosion hazard of this compound in the laboratory and in industrial applications:
1. Keep reaction temperatures involving chlorine dioxide as low as possible.

2. Avoid contact with or contamination by organic compounds.

3. Dilute gas and/or solid reactants with inert materials. Explosion hazard is substantially reduced if concentration of the gas is maintained at less than 10 per cent (37).

4. Avoid storage and/or accumulations of the compound. Use as soon as possible after preparation, and do not prepare more than can reasonably be expected to be used.

Photochemical Decomposition. Chlorine dioxide absorbs light of 3650 A. wave length, and two molecules of the compound are photochemically decomposed for each quantum of energy absorbed. Action of light produces an initial decrease in pressure, and a red liquid (Cl$_2$O$_6$) forms on the walls of the container. For a dry, gaseous system the mechanism of photochemical decomposition is represented by the following equations:

1. ClO$_2$ + h$\nu$ $\rightarrow$ [ClO]/ + O, the primary step

then, 2. ClO$_2$ + O $\rightarrow$ ClO$_3$,

and 3. 2[ClO]/ $\rightarrow$ Cl$_2$ + O$_2$.

The ClO$_3$ which has been produced can then undergo either of the two reactions:

4. 2ClO$_3$ $\rightarrow$ Cl$_2$O$_6$, forming the red liquid,

and/or 5. 2ClO$_3$ $\rightarrow$ Cl$_2$ + 3O$_2$, a thermal decomposition reaction.

Reaction 5 above has a high activation energy, therefore, a high temperature coefficient. As the temperature is lowered, this reaction becomes less important allowing more of the hexoxide (the red liquid) to be formed as is observed experimentally.

With moist gas, no chlorine gas appears in the products; but a complicated mixture of acids - hypochlorous (HClO), chlorous (HClO$_2$), chloric (HClO$_3$), and perchloric (HClO$_4$) - is found in the reaction "mist". Again light of 3650 A. is absorbed, and the primary step in the decomposition is the same as with the dry gas. This mechanism for decomposition with moist gas is described by the following series of reactions:

1. ClO$_2$ + h$\nu$ $\rightarrow$ [ClO]/ + O, the primary step,

and ClO$_3$ and the hexoxide are formed as before

2. ClO$_2$ + O $\rightarrow$ ClO$_3$

3. 2ClO$_3$ $\rightarrow$ Cl$_2$O$_6$.
These materials can then interact with water:

4. \( \text{Cl}_2\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{HClO}_3 + \text{HClO}_4 \),

5. \( [\text{ClO}] + \text{ClO}_2 \rightarrow \text{Cl}_2\text{O}_3 \),

6. \( [\text{Cl}_2\text{O}_3] + \text{H}_2\text{O} \rightarrow 2\text{HClO}_2 \rightarrow \text{HClO} + \text{HClO}_3 \).

If the photochemical decomposition is carried out in a solution of an inert solvent, i.e., carbon tetrachloride, a still different mechanism is followed and has been discussed by Schumacher (33). Bowen (6) and Nagai and Goodeve (25) reported that none of the unstable intermediates react with solvent molecules, the quantum yield for light absorption up to 4200 Å. wavelength is 2.0 decreasing quickly to unity at 436 μm, and also that no chlorine hexoxide is formed under these conditions. While the mechanism is not well understood in solution, Schumacher believes the primary step to be

1. \( \text{ClO}_2 + h\nu \rightarrow \text{Cl} + \text{O}_2 \)

followed by 2. \( \text{Cl} + \text{ClO}_2 \rightarrow \text{Cl}_2 + \text{O}_2 \).

In the case of the gaseous reaction, the products of the primary step immediately following the decomposition of the activated \( \text{ClO}_2 \) molecule were \( \text{ClO} \) and \( \text{O}_2 \), both with excess energy. Since these products possessed excess energy it is reasonable that they fly apart, not remaining together long enough to form a chlorine atom and an oxygen molecule. When the decomposition is carried out in solution, however, where molecules can much more easily give up excess energy to solvent molecules and also where the mean free path is much shorter, there is a much greater probability for the \( \text{ClO} \) and \( \text{O}_2 \) which were produced in the previously discussed primary step to produce \( \text{Cl} \) and \( \text{O}_2 \) as indicated. The lack of oxygen atoms precluded the existence of the hexoxide since in all previous discussions this compound was only produced by the two reactions

\( \text{ClO}_2 + \text{O} \rightarrow \text{ClO}_3 \)

followed by \( 2\text{ClO}_3 \rightarrow \text{Cl}_2\text{O}_6 \).

Spinks and Taube (38) have examined the bromine-sensitized decomposition of chlorine dioxide in carbon tetrachloride solution and found that in this case substantial amounts of chlorine hexoxide were obtained.

**Thermal Decomposition.** The thermal decomposition of chlorine dioxide has been rather extensively studied by Steiger and Schumacher (33,34) and reviewed by Semenoff (35). This reaction has a number of differences from the similar reaction of chlorine monoxide. The dioxide decomposes by a heterogeneous mechanism, the nature of the surface and the surface to volume ratio having a strong and not completely understood influence on the reaction velocity. Increasing the total pressure also increases the reaction rate. The reaction proceeds at a measurable rate at 30°C., increasing to explosive proportions at 50° to 60°C. The temperature coefficient of the
reaction rate varies from vessel to vessel, but at 40°C. the rate increases by a factor of about 5 per 10°C. temperature increase.

The course of the reaction is revealed by pressure changes. The rate increases through an initial induction period, passes through a maximum, after which the rate falls, remaining almost constant as shown by curve II of figure 2. Under some conditions an explosive reaction is obtained as in curve III.

Schumacher uses a chain reaction mechanism to explain the decomposition with the chain initiation step,

1. \( \text{ClO}_2 \xrightarrow{\text{wall}} [\text{ClO}] + 0 \),

occurring on the wall of the reaction vessel. While this reaction is endothermic by 60 kcal./mole, it is believed that it does occur to some extent on the walls. As shown before, ClO decomposes to chlorine and oxygen

2. \( [\text{ClO}] \rightarrow \text{Cl}_2 + 0_2 \),

but the oxygen atoms, which are being slowly produced on the wall, react by the process

3. \( 0 + \text{ClO}_2 \rightarrow \text{ClO}_3 \).

The ClO\(_3\) which is produced then reacts with dioxide according to two processes, one a chain propagating reaction

4. \( \text{ClO}_3 + \text{ClO}_2 \rightarrow \text{Cl}_2 + 20_2 + 0 \)

and a chain breaking reaction

5. \( \text{ClO}_3 + \text{ClO}_2 \xrightarrow{\text{wall}} \text{Cl}_20 + 20_2 \).

Additions of such gases as oxygen, chlorine (see curve IV, figure 2), carbon dioxide, etc. increase the reaction velocity simply by increasing the total pressure. Addition of either Cl\(_2\)O or CO has an inhibiting influence on the decomposition. Carbon monoxide breaks chains by consuming oxygen atoms, but the mechanism by which Cl\(_2\)O retards the reaction is not well understood. This observation is in agreement with the explanation for the explosion at the end of the decomposition reaction of chlorine monoxide.

The thermal decomposition reaction involves a mechanism whereby the chains are initiated and terminated on the vessel walls. Since two wall reactions are involved each with different temperature coefficients and with different number and types of reaction sites, it is not surprising that the nature of the surface and its geometry have a marked influence on the
course of the reaction. The different behavior of the reaction in quartz and glass reactors is shown by curves II and III of figure 2. Schumacher and Steiger (34) describe an experiment in a particular quartz vessel in which decomposition was complete in 2 or 3 hours at 45°C. After this vessel had been washed with potassium iodide solution, thoroughly rinsed in distilled water, and vacuum dried, no reaction occurred during 12 hours at 45°C. Slight decomposition was detectable after 2 hours at 50°C; and only 1/2 hour after reaching 56°C., a violent explosion occurred which destroyed the vessel.

Other Chemical Properties. Chlorine dioxide is quite soluble in water and forms a hydrate, ClO₂•5H₂O, which is stable up to 18°C. The aqueous solutions are stable at low temperatures, if kept in the dark, and the dioxide can be expelled from the solution even after a long storage time. Decomposition occurs in the light by the reaction

\[ 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}_3 + \text{O}_2. \]

In alkaline solution, reaction produces a chlorite and a chlorate, thus,

\[ 2\text{ClO}_2 + 2\text{NaOH} \rightarrow \text{NaClO}_2 + \text{NaClO}_3 + \text{H}_2\text{O}. \]

In the presence of a reducing agent the above reaction produces only a chlorite.

Reaction of chlorine dioxide with fluorine can be explosive producing chlorine and oxygen or, under suitable conditions, chloryl fluoride. This reaction will be discussed later.

Chlorine Hexoxide

Chlorine hexoxide, a red liquid, exists as a dimer, Cl₂O₆, in the liquid phase and as a monomer, ClO₃, in the vapor phase. The physical properties are summarized in table II. The vapor pressure was measured over the range -40° to +20°C. by Goodeve and Richardson (19). The equation expressing the vapor pressure of the liquid is

\[ \log P_{\text{mm}} = 7.1 - \frac{2070}{T}, \]

and of the solid is

\[ \log P_{\text{mm}} = 9.3 - \frac{2690}{T}. \]

The equilibrium constant for the reaction,

\[ \text{Cl}_2\text{O}_6 \Leftrightarrow 2\text{ClO}_3, \]

has been measured by making use of the magnetic properties of the trioxide. Since ClO₃ contains an odd number of electrons, it has an unpaired electron and is therefore paramagnetic; whereas Cl₂O₆ has an even number and is
diamagnetic. From consideration of magnetic measurements, the equilibrium constant, \( K_c \), has been found to obey the equation

\[
\log K_c = -0.974 - \frac{278}{T}.
\]

The heat of this dissociation reaction is only 1730 cal./mole indicating very weak bonds between the ClO\(_2\) monomers. Since the bond is so weak, no break in the \( \log K_c \) vs. \( 1/T \) plot is observed at the melting point, and the Trouton constant has its normal value in spite of the association reaction.

**Preparation.** Chlorine hexoxide is known to be a long-lived intermediate in the thermal and photochemical decomposition of chlorine dioxide. This red liquid was observed as early as 1843, but the composition of the material was not identified until 1925 \( ^4 \) when the chlorine to oxygen ratio was found to be three.

Chlorine hexoxide is also a product of the action of ozone on chlorine and chlorine dioxide. This reaction with the dioxide,

\[
2\text{ClO}_2 + 2\text{O}_3 \longrightarrow \text{Cl}_2\text{O}_6 + 2\text{O}_2,
\]

is the best method of preparation. The kinetics of the photochemical reaction of chlorine and ozone have been studied \( ^5 \) at 35° and 50°C. with the following mechanism formulated to explain these kinetic results. The primary step is activation of the ozone molecule by absorption of blue light of wave length about 4700 Å. An energy rich molecule, \( \text{O}_3^* \), is formed

1. \( \text{O}_3 + h\nu \longrightarrow \text{O}_3^* \),

followed by the reaction

2. \( \text{O}_3^* + \text{Cl}_2 \longrightarrow [\text{ClO}] + \text{ClO}_2 \).

As noted earlier, ClO is unstable and decomposes rapidly by the reaction

3. \( 2[\text{ClO}] \longrightarrow \text{Cl}_2 + \text{O}_2 \).

The dioxide can also react with ozone even in the absence of light,

4. \( \text{ClO}_2 + \text{O}_3 \longrightarrow \text{ClO}_3 + \text{O}_2 \),

producing ClO\(_3\) which condenses as a red liquid,

5. \( 2\text{ClO}_3 \longrightarrow \text{Cl}_2\text{O}_6 \).

The major complication in this reaction scheme is that chlorine trioxide undergoes other reactions with ozone resulting in decomposition \( ^{29} \). Reaction 4 above may result in an energy rich molecule, ClO\(_3^*\), which can
lose its excess energy in a number of ways. The energy loss may occur simply as conversion to kinetic energy by collisions which do not yield chemical reactions, or it may be lost to a wall. If the energy rich molecule collides with ozone, the following reactions may occur:

\[
\begin{align*}
6. \quad & \text{ClO}_3^* + O_3 \rightarrow \text{ClO}_2 + 2O_2 \\
7. \quad & \text{ClO}_3^* + O_3 \rightarrow \text{ClO}_4^+ + O_2 .
\end{align*}
\]

The ClO$_4^+$ leads to formation of Cl$_2$O$_7$ and will be discussed later. Dilution of the gases with nitrogen, chlorine, oxygen, etc., or increase of the surface area of the reaction vessel decreases the probability of collisions between ClO$_x^*$ and ozone, thus inhibiting reactions 6 and 7. The activation energy for reaction 6 was found to be 10.9 kcal./mole, which is equivalent to a temperature coefficient of about 2 for a 10°C temperature rise.

**Thermal Decomposition.** Thermal decomposition of the trioxide (or hexoxide) is measurable in the temperature range 0°C to 30°C and constitutes a further complication to the ozone reaction discussed above. Thermal decomposition was studied by Burns and Rollefson (27), and two reactions were noted; namely,

\[
\begin{align*}
1. \quad & 2\text{ClO}_3 \rightarrow \text{Cl}_2 + 3O_2 \\
2. \quad & 2\text{ClO}_3 \rightarrow 2\text{ClO}_2 + O_2 .
\end{align*}
\]

By observation of pressure change in the temperature range 0°C to 30°C, it was found that below 10°C decomposition follows reaction 2, but 1 has a higher activation energy. At 30°C, they both proceed at about equal rates. For preparative purposes, the best yields were obtained by maintaining the temperature at 0°C or below. It should be recognized that the hexoxide can decompose explosively, and there is no really safe method of handling the compound.

**Other Reactions.** Chlorine hexoxide reacts violently, sometimes explosively, with water producing chloric and perchloric acids according to the reaction

\[
\text{Cl}_2\text{O}_6 + H_2O \rightarrow \text{HClO}_3 + \text{HClO}_4 .
\]

In alkaline solution, chlorates and perchlorates are obtained. As expected, explosive reactions can be obtained with organic materials.

The reaction of chlorine hexoxide and fluorine has recently been studied by Davila (12) and found to be highly exothermic. The products obtained were 70 to 75% chloryl fluoride (ClO$_2$F), 20 to 25% chlorine heptoxide (Cl$_2$O$_7$), 1 to 3% chlorine, and a trace of fluorine perchlorate (FClO$_4$). The proposed mechanism may be written

\[
1. \quad \text{Cl}_2\text{O}_6 \rightarrow 2\text{ClO}_3 ,
\]
2. \(2\text{ClO}_3 \rightarrow \text{ClO}_2 + [\text{ClO}_4]\),

followed by fluorination or recombination reactions; thus,

3. \(\text{ClO}_2 + \text{F}_2 \rightarrow \text{ClO}_2\text{F} + \text{F}\),

4. \([\text{ClO}_4] + \text{ClO}_3 \rightarrow \text{Cl}_2\text{O}_7\),

5. \(\text{F} + [\text{ClO}_4] \rightarrow \text{FCIO}_4\).

While the temperature was not stated, the reaction was probably carried out below 0°C.

### Chlorine Heptoxide

The physical properties of chlorine heptoxide are outlined in table II. One observes a regular increase in melting point (figure 3) as the oxygen to chlorine ratio increases from chlorine monoxide to dioxide to hexoxide. The chlorine heptoxide melting point is much lower than one would anticipate from the correlation. Maxted (21) attributes this deviation to the molecular structure of the heptoxide (table II) which is nonplanar and contains a peroxide linkage between \(\text{ClO}_2\) groups. This nonplanar structure prevents a tight, closely arranged crystal structure, as is obtained with the hexoxide, allowing the crystal lattice to decompose or the compound to melt at a much lower temperature.

**Preparation.** Dehydration of perchloric acid yields chlorine heptoxide. This dehydration may be carried out with phosphorous pentoxide and the reaction is complete in about 1 day at -10°C. (23). Goodeve and Powney (18) have carried out the reaction at higher temperatures and obtained good yields.

Chlorine heptoxide is also a product of the photochemical reaction of ozone with chlorine dioxide. Lower temperatures favor the formation of chlorine hexoxide, but higher temperatures (30°C.) favor the formation of the heptoxide. It was shown in the chlorine hexoxide discussion that this compound may undergo reaction with ozone - even in the dark - to produce an energy rich chlorine trioxide. The energy rich molecule may lose its excess energy by any of the following reactions (7):

1. \(\text{ClO}_3^* + \text{wall} \rightarrow \text{ClO}_3 + \text{wall}\),

2. \(\text{ClO}_3^* + \text{M} \rightarrow \text{ClO}_3 + \text{M} + \text{kinetic energy}\),

3. \(\text{ClO}_3^* + \text{O}_3 \rightarrow \text{ClO}_2 + 2\text{O}_2\),

and/or

4. \(\text{ClO}_3^* + \text{O}_3 \rightarrow [\text{ClO}_4] + \text{O}_2\).

In reaction 2, \(\text{M}\) may be any molecule, even ozone, but a portion of the ozone collisions proceeds by equations 3 and 4. Reaction 4 takes place at
MELTING POINTS OF THE CHLORINE OXIDES

FIGURE 3
the higher temperature, producing the unstable intermediate, ClO$_4^-$, which
then produces chlorine heptoxide by the reaction

$$5. \ [\text{ClO}_4^-] + \text{ClO}_3^- \rightarrow \text{Cl}_2\text{O}_7$$

This constitutes a chain terminating reaction since chlorine heptoxide is
relatively stable - in comparison to the life of the many intermediates -
and slowly builds up in concentration until condensation to the liquid
takes place.

Other Reactions. Chlorine heptoxide is the most stable of the chlorine
oxides, yet it can explode violently on shock or sudden heating. The
liquid slowly decomposes at room temperature producing chlorine and oxygen,
but the detailed mechanism and kinetics have not been worked out.

The slow reaction of chlorine heptoxide with water was studied by Goodeve
and Marsh (17) during their determination of the heat of formation of
perchloric acid. While the heptoxide vapor fumes in contact with ordinary
air, it is surprising that when liquid heptoxide is added to water, it
sinks to the bottom of the vessel and only slowly goes into solution. It
has been suggested that there is a limited solubility of perchloric acid
in the heptoxide and that a film of perchloric acid builds up on the liquid
droplet allowing further reaction to proceed only by diffusion through the
film. This situation is quite different from the violent reaction obtained
when chlorine hexoxide reacts with water.

Chloryl Fluoride

The physical properties of chloryl fluoride are outlined in table II.

Preparation. This compound was first prepared by Schmitz and Schumacher (32)
by direct fluorination of chlorine dioxide. While fluorine and chlorine
dioxide normally explode when brought together, under controlled conditions
one obtains chloryl fluoride. In a reactor at -36°C., containing 50 mm.
Hg pressure of ClO$_2$, Schmitz and Schumacher found that careful addition of
80 mm. partial pressure of fluorine produced some chloryl fluoride in 30
minutes. If the fluorine concentration were increased to 130 mm., an
explosion resulted. In order to decrease the reaction time, the temperature
was raised to 0°C.; but using 50 mm. chlorine dioxide and 50 mm. fluorine
partial pressure, an explosion was produced even when these gases were
diluted with air. By reducing the chlorine dioxide pressure to 25 mm.,
keeping the fluorine at 50 mm., and again diluting with air, it was possible
to obtain chloryl fluoride with a reaction time of 2 or 3 minutes.

More recently (1) the kinetics of the gas phase reaction of fluorine and
chlorine dioxide have been studied in the temperature range -46° to -26°C.
and the pressure range 50 to 500 mm. Hg. The rate of formation of chloryl
fluoride obeyed the equation
where $k_1$ had the following values:

- 0.23 liter (mole sec.)$^{-1}$ at $-46^\circ C$.
- 0.52 liter (mole sec.)$^{-1}$ at $-36^\circ C$.
- 1.05 liter (mole sec.)$^{-1}$ at $-26^\circ C$.

The following mechanism was proposed:

1. $F_2 + ClO_2 \rightarrow ClO_2F + F$,
2. $F + ClO_2 \rightarrow FCIO_2$,
3. $F + F + M \rightarrow F_2 + M$,
and
4. $2F \rightarrow F_2$.

Reactions 1 and 4 were the most important with 2 and 3 only contributing significantly when the chlorine oxide pressure or the total pressure was high. The relative contribution of reaction 2 was increased by increasing the temperature, and reaction 1 was found to be an entirely homogeneous gas phase process.

A solution of chlorine dioxide in an inert solvent such as Freon-11 ($CCl_3F$) will yield chloryl fluoride when fluorine is bubbled through the liquid. Other preparative methods are as follows: a stream of chlorine dioxide diluted with nitrogen and passed over $AgF_2$ at room temperature, bubbling chlorine dioxide through bromine trifluoride at $30^\circ C.$, and passing $NO_2F$ through a Freon solution of chlorine hexoxide at $0^\circ C.$ (31).

Chemical Properties. The chemical reactions of chloryl fluoride have not been studied extensively. Its behavior toward moisture indicates a reactive fluorine atom since dense white fumes of hydrogen fluoride are obtained upon exposure to moist air. If the gas is admitted to wet silica apparatus one obtains upon hydrolysis reddish brown vapors (probably chlorine monoxide and dioxide). Some workers (32) have observed that chloryl fluoride reacts with glass, but have been successful in handling the compound in silica equipment. The thermal stability of the compound has not been studied, but it appears to be much more stable than chlorine dioxide.

Chloryl fluoride undergoes an addition-type reaction as illustrated by the following equations (10,31):

\[
ClO_2F + SbF_5 \rightarrow ClO_2SbF_6 \text{ (melting point +78}^\circ C.)
\]

or

\[
6ClO_2F + SbCl_5 \rightarrow 5ClO_2 + 5/2Cl_2 + ClO_2SbF_6
\]

and with silicon tetrafluoride one obtains $(ClO_2)_2SiF_6$. It has been
reported that a similar addition product forms with vanadium pentafluoride below \(-46^\circ C\), but the compound decomposes at room temperature. With fluorosulphonic acid the reaction is

\[
\text{C}_1\text{O}_2\text{F} + \text{HSO}_3\text{F} \xrightarrow{\text{\(-78^\circ C\)}} \text{HF} + \text{C}_1\text{O}_2\text{SO}_3\text{F}.
\]

It appears that this addition type reaction is a general one for chloryl fluoride and that it might react with many other compounds as yet unidentified.

The reactions with hydrogen chloride and anhydrous nitric acid are different from the straight-forward addition type reaction. These reactions are:

\[
\text{C}_1\text{O}_2\text{F} + \text{HCl} \text{ (anhyd.)} \xrightarrow{\text{\(-110^\circ C\)}} \text{HF} + \text{C}_1\text{O}_2 + \frac{1}{2} \text{Cl}_2
\]

and

\[
2\text{C}_1\text{O}_2\text{F} + 2\text{HNO}_3 \text{ (anhyd.)} \xrightarrow{\text{\(-30^\circ C\)}} 2\text{HF} + \text{NO}_2\text{ClO}_4 + \text{NO}_2 + \text{ClO}_2
\]

Because of the nature of the products, one should expect explosions when chloryl fluoride contacts either of these acids.

**Perchloryl Fluoride**

Perchloryl fluoride was first reported in 1951, and even though it is the newest of the compounds discussed in this report, its physical properties are the most thoroughly studied of the chlorine oxyfluorides. Because of the strong oxidizing power coupled with its great stability, perchloryl fluoride is a potentially useful chemical intermediate. A very large amount of the information available on this compound has been obtained and/or compiled by the technical organization of the Pennsalt Chemicals Corporation \((27)\) which company produces the compound on an industrial scale. In addition to the physical properties outlined in table II, other properties are listed in table III.
TABLE III
ADDITIONAL PHYSICAL PROPERTIES OF PERCHLORYL FLUORIDE

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical Temperature</td>
<td>95.17 ± 0.10°C.</td>
</tr>
<tr>
<td>Critical Pressure</td>
<td>53.00 atm.</td>
</tr>
<tr>
<td>Critical Density</td>
<td>0.637 g./ml.</td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>0.03 Debye units</td>
</tr>
<tr>
<td>Viscosity of Liquid</td>
<td>0.620 centipoise at -80°C.</td>
</tr>
<tr>
<td></td>
<td>0.219 centipoise at 0°C.</td>
</tr>
<tr>
<td></td>
<td>0.139 centipoise at 60°C.</td>
</tr>
<tr>
<td>Specific Heat of Liquid</td>
<td>23.5 cal./mole at -40°C.</td>
</tr>
<tr>
<td></td>
<td>25.0 cal./mole at -10°C.</td>
</tr>
<tr>
<td></td>
<td>29.7 cal./mole at 50°C.</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>24.05 dynes/cm. at -75.2°C.</td>
</tr>
<tr>
<td></td>
<td>22.31 dynes/cm. at -65.9°C.</td>
</tr>
<tr>
<td></td>
<td>21.25 dynes/cm. at -55.7°C.</td>
</tr>
<tr>
<td>Vapor Pressure,</td>
<td>( \log \frac{p_{\text{mm. Hg}}}{\text{mm. Hg}} = 18.90112 - \frac{1443.467}{T} - 4.09566 \log T )</td>
</tr>
<tr>
<td>-120° to -40°C.</td>
<td></td>
</tr>
<tr>
<td>Vapor Pressure,</td>
<td>( \log \frac{p_{\text{atm.}}}{\text{atm.}} = 4.46862 - \frac{1010.814}{T} )</td>
</tr>
<tr>
<td>-40° to 95.17°C.</td>
<td></td>
</tr>
<tr>
<td>Density of Saturated</td>
<td>( (\text{g./ml.}) = 1.088 - 7.280 \times 10^{-4}T + 6.455 \times 10^{-2}(T_c - T)^{1/2} )</td>
</tr>
<tr>
<td>Liquid,</td>
<td></td>
</tr>
<tr>
<td>-142° to 54°C.</td>
<td></td>
</tr>
</tbody>
</table>

Preparation. Quantity preparations of perchloryl fluoride appear to involve fluorination of a chlorate or a perchlorate. Engelbrecht and Atzwanger (13) outline the mechanism of fluorination of potassium chlorate at various temperatures in the following manner.
KC1O$_3$ + 1/2 F$_2$ $\rightarrow$ (ClO$_3$) + KF

\[ + 1/2 F_2 \] 40° to 20° C.

\[ \rightarrow \] 40° to 60° C.

\[ \rightarrow \] Cl$_2$O$_6$

CLO$_3$F

CLO$_2$ + 1/2 O$_2$

\[ + 1/2 F_2 \] 100° C.

O$_2$ + 1/2 Cl$_2$ $\rightarrow$ ClF

At 100° C., 45% of the fluorine is consumed to produce CLO$_2$F. As the temperature is increased, less perchloryl fluoride is obtained and greater quantities of chloryl fluoride and chlorine appear.

Barth-Wehrenalp (2) has prepared perchloryl fluoride by the action of fluorosulfonic acid on potassium perchlorate in 67% yield. This reaction has the advantage that elemental fluorine is not required (fluorosulfonic acid is made with hydrogen fluoride and sulfuric acid or sulfur trioxide) and that a complex, (CLO$_2$)$_2$S$_2$O$_10$, is formed with chlorine dioxide which allows the slow, controlled decomposition of chlorine dioxide.

Chemical Properties. Perchlooryl fluoride is thermally stable up to 500° C., and it is much more resistant to hydrolytic attack than other chlorine oxyfluorides, hydrolysis at 250° to 300° C. being a slow reaction. In an alkaline environment, however, the reactivity increases markedly; and alcoholic potassium hydroxide causes rapid hydrolysis even at 25° C. It is not corrosive to most metals - aluminum, copper, nickel or steel - in the anhydrous state; but the moist gas is severely corrosive to aluminum and steel. The compound reacts with organic compounds in three ways: 1) as an oxidizing agent, 2) as an acid fluoride requiring alkaline reagents to initiate reaction, and 3) as a "Lewis base" in Friedel-Crafts type reactions. At 250° to 350° C., most organic compounds will react by one of the above mechanisms, in some cases with explosive velocities. At room temperature, however, reactivity is sufficiently slow so that solubility values, given in table IV, could be measured.
TABLE IV

SOLUBILITY OF PERCHLORYL FLUORIDE VAPOR IN VARIOUS SOLVENTS

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Approximate Solubility (g./l.) at 25°C. and 760 mm. Hg pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.6</td>
</tr>
<tr>
<td>Carbon Tetrachloride</td>
<td>1.6</td>
</tr>
<tr>
<td>Ether</td>
<td>2.3</td>
</tr>
<tr>
<td>Ethanol or Acetone</td>
<td>2.5</td>
</tr>
<tr>
<td>Methanol or Ethyl Acetate</td>
<td>2.6</td>
</tr>
<tr>
<td>Benzene or Acetic Acid</td>
<td>2.7</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>3.9</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.3</td>
</tr>
<tr>
<td>Dioxane</td>
<td>5.0</td>
</tr>
</tbody>
</table>

In the gas phase, perchloryl fluoride will oxidize hydrogen chloride at 200°C. according to the reaction

\[ \text{C}_{10}\text{F}_7 + 7 \text{HCl} \rightarrow \text{HF} + 4 \text{Cl}_2 + 3 \text{H}_2\text{O} , \]

and it undergoes a strongly exothermic reaction with anhydrous aluminum chloride. With ammonia gas the following reaction takes place:

\[ \text{C}_{10}\text{F}_7 + 3 \text{NH}_3 \rightarrow \text{NH}_4\text{F} + \text{C}_{10}\text{NH-NH}_4 , \]

producing perchlorylamide, again indicating its reactivity toward alkaline reagents. Metallic salts of this compound may be formed and may detonate when dry. It is reported that the gas will support combustion as rapidly as oxygen.

Fluorine Perchlorate

Fluorine perchlorate is by far the most explosive of the chlorine oxyfluorides; and for this reason, relatively little is known about the compound. It was first prepared by Rohrback and Cady (28); and the complete knowledge of the compound is contained in their paper. The physical properties are presented in table II.

The preparation of the compound was achieved by the action of fluorine on 72% perchloric acid at 21°C. in a platinum boat. The initial stages of the reaction involved elimination of water by the reactions,

\[ 2 \text{H}_2\text{O} + 2\text{F}_2 \rightarrow \text{O}_2 + 4 \text{HF} \]

and

\[ \text{H}_2\text{O} + 2\text{F}_2 \rightarrow \text{OF}_2 + 2 \text{HF} , \]
but continued fluorination produced fluorine perchlorate in 90% yield.

Some information on the chemical properties is revealed by the analytical procedure used by Rohrback and Cady. On careful addition of fluorine perchlorate gas to 1% potassium iodide solution, one mole of iodine was liberated for each mole of gas used,

\[ \text{ClO}_4^F + 2\text{I}^- \rightarrow \text{I}_2 + \text{ClO}_4^- + \text{F}^- . \]

The reaction with sodium hydroxide solution proceeded by the equation

\[ 2 \text{ClO}_4^F + 4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{ClO}_4^- + 2 \text{F}^- + 2 \text{H}_2\text{O} . \]

The compound is reported to be very easily exploded; either a small flame or spark would cause a detonation which would shatter an open-ended glass test tube containing the gas. Contact with organic matter, and even the process of solidification of the compound at the freezing point, frequently resulted in explosions.

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BIBLIOGRAPHY


