Portland State University

PDXScholar

Dissertations and Theses

Dissertations and Theses

4-16-1976

The Chemistry of Chromium (VI) And Chromium (V) Oxide Fluorides

Patrick Jay Green

Portland State University

Follow this and additional works at: https://pdxscholar.library.pdx.edu/open_access_etds

Part of the [Chemistry Commons](#)

Let us know how access to this document benefits you.

Recommended Citation

Green, Patrick Jay, "The Chemistry of Chromium (VI) And Chromium (V) Oxide Fluorides" (1976).
Dissertations and Theses. Paper 4039.
<https://doi.org/10.15760/etd.5923>

This Thesis is brought to you for free and open access. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

AN ABSTRACT OF THE THESIS OF Patrick Jay Green for the Master of Science in Chemistry presented April 16, 1976.

Title: Chemistry of Chromium(VI) and Chromium(V) Oxide Fluorides.

APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

[REDACTED]

Gary L. Gard, Chairman

[REDACTED]

Morris B. Silverman

[REDACTED]

Dennis W. Barnum

[REDACTED]

Edward M. Perdue

New preparative routes to chromyl fluoride were sought. It was found that chlorine monofluoride reacts with chromium trioxide and chromyl chloride to produce chromyl fluoride. Attempts were made to define a mechanism for the reaction of ClF and CrO_3 in light of by-products observed and previous investigations. Carbonyl fluoride and chromium trioxide react to form chromyl fluoride and carbon dioxide. A mechanism was also proposed for this reaction. Chromium trioxide with MoF_6 or WF_6 reacts to produce chromyl fluoride and the respective oxide tetrafluoride.

Sulfur hexafluoride did not react with CrO_3 .

A limited study of the reaction chemistry of chromyl fluoride was undertaken. The interaction of NO_2F and NOF and CrO_2F_2 leads to nitronium and nitrosonium trifluorochromate(VI) salts, respectively. The structure of these compounds was assigned as a cis-dioxo, fluorine bridged polymer on the basis of infrared spectral data and its similarity to previously reported work where the structures were confirmed by x-ray crystallography. The previously reported compound, $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$, was found to form a 1:2 adduct with acetonitrile which was shown from infrared spectral data to contain coordinated CH_3CN groups. Chromyl fluoride was found to react with n-hexane to form an Etard complex of non-stoichiometric composition. The infrared spectrum of the complex displayed a band which was assigned to a carbonyl group coordinated to a chromium center. Hydrolysis of the complex produced ten different organic compounds, among which hexanoic acid, 2-hexanone, and 3-hexanone were identified. Tetrachloroethylene, trifluoroethylene, and 1,1-difluoroethylene were found to react with chromyl fluoride with only 1,1-difluoroethylene yielding a stoichiometric complex, $\text{CF}_2\text{:CH}_2 \cdot 2\text{CrO}_2\text{F}_2$. The solid products of the reactions of all three olefins with CrO_2F_2 show an infrared band which was assigned to a carbonyl group coordinated to chromium, like the n-hexane Etard complex. Hydrolysis of $\text{CF}_2\text{:CH}_2 \cdot 2\text{CrO}_2\text{F}_2$ does not yield trifluoroethanol as had been reported.

It was found that CrO_3 or CrO_2F_2 react with excess ClF at 100° to form a red-brown solid which was found to correspond to a composition of $\text{CrOF}_3 \cdot 0.14\text{ClF}$ to $\text{CrO}_2\text{F}_2 \cdot 0.21\text{ClF}$. Treatment of this solid with F_2 at 120°

or reaction of ClF and CrO_2F_2 at 250° leads to a nonvolatile purple solid which was found to be greatly depleted in chlorine. This purple CrOF_3 was assigned to be a fluorine-bridged polymer with terminal chromium-oxygen double bonds from infrared and Raman spectral information. Chromium oxide trifluoride reacts with fluorine at 180° to form CrF_5 and with antimony pentafluoride to produce $\text{CrOF}_3 \cdot 2\text{SbF}_5$.

THE CHEMISTRY OF CHROMIUM(VI) AND CHROMIUM(V) OXIDE FLUORIDES

by

PATRICK JAY GREEN

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

in

CHEMISTRY

Portland State University
1976

TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the thesis of
Patrick Jay Green presented April 16, 1976.

Gary L. Gard, Chairman

Morris B. Silverman

Dennis W. Barnum

Edward M. Perdue

APPROVED:

Gary L. Gard, Head, Department of Chemistry

Richard B. Halley, Dean of Graduate Studies and Research

TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	iv
LIST OF TABLES	v
CHAPTER	
I Experimental.....	1
II New Preparations of Chromyl Fluoride	10
III Some Reaction Chemistry of Chromyl Fluoride	30
IV Preparation and Characterization of Chromium(V) Oxide Trifluoride	67
BIBLIOGRAPHY	91

ACKNOWLEDGEMENTS

The author wishes to thank Mr. Steven Brown for assistance in obtaining Raman spectral data and for many productive discussions, Dr. Thomas Loehr of the Oregon Graduate Center for use of the Raman spectrometer, Ms. An McFarlane for typing the manuscript, Dr. Gary Gard for his patience, overall help and advice, and his wife, Susan, for her unvarying support.

LIST OF FIGURES

FIGURE		PAGE
1	Chromyl Fluoride Etard Reaction Apparatus	6
2	Proposed Mechanism of the Reaction of Chlorine Monofluoride and Chromium Trioxide at 0° ..	23
3	Proposed Mechanism of the Reaction of Carbonyl Fluoride and Chromium Trioxide	24
4	Structure of the MO_2F_3^- ion ($\text{M} = \text{V}, \text{W}, \text{Mo}$)....	45
5	Structures of Metal Oxide Trihalides	82

LIST OF TABLES

TABLE		PAGE
I	Physical Properties of Chromyl Fluoride	11
II	Previously Reported Preparations of Chromyl Fluoride	11
III	New Preparations of Chromyl Fluoride	12
IV	Reactions of Molybdenum and Tungsten Hexafluorides	15
V	Proposed Explanation of the Reaction of Chromium Trioxide and Chlorine Monofluoride at 0°C...	26
VI	Infrared Absorbances (in cm^{-1}) of Volatile Products of the Reaction of CrO_3 and ClF at 0°C.....	27
VII	Bond Lengths and Angles of Chromyl Fluoride.....	31
VIII	Chromyl Chloride Oxidation Products	34
IX	Infrared Vibrational Frequencies of $\text{NO}_2\text{CrO}_2\text{F}_3$ and NOCrO_2F_3	47
X	Infrared Vibrational Frequencies of $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$ and Related Molecules	51
XI	Vibrational Frequencies of the n-Hexane Etard Complex	55
XII	Infrared Absorbances of n-Hexane Etard Hydro-sylate	58
XIII	Vibrational Frequencies of Chromyl Fluoride-ChloroFluoroolefin Reaction Products	63
XIV	Vibration Frequencies of Selected Chlorine Ions and ClF	75
XV	Observed Vibrational Frequencies of $\text{CrOF}_3 \cdot 0.21 \text{ ClF}$	76
XVI	X-Ray Powder Patterns of CrOF_3 Prepared by Two Methods	78

TABLE		PAGE
XVII	X-Ray Powder Patterns of Products Obtained from Thermal Decomposition of CrOF_3 and Reaction of CrO_3 and ClF at 285°	80
XVIII	Metal-Oxygen Stretching Frequencies for Solid Transition Metal Oxide Trihalides	83
XIX	Vibrational Frequencies of CrOF_3 , VOF_3 , and MoOF_3	85
XX	Electronic Spectrum of the Product of CrOF_3 and SbF_5 and Other Cr(V) Compounds	88
XXI	Vibrational Frequencies of $\text{CrO}_2\text{FSb}_2\text{F}_{11}$ and $\text{CrF}_4\text{Sb}_2\text{F}_{11}$	90

CHAPTER I

EXPERIMENTAL

Physical Methods

Infrared Spectra. Infrared spectra reported in this work were recorded on Perkin-Elmer Model 467 infrared spectrophotometer over the range 4000 to 250 cm^{-1} . Spectra of gases were obtained using a Monel gas cell (AgCl windows) with a path length of 8.25 cm. The cell was equipped with a Whitey brass valve and metal 10/30 $\frac{1}{8}$ joint to adapt to the vacuum system. Solid product spectra were obtained either as nujol mulls or neat between CsBr or KRS-5 plates. A KBr minipress was also used for solid spectra. Infrared spectra were calibrated using polystyrene film.

Raman Spectra. Raman spectra reported in this work were recorded on a Jarrell Ash 25-300 Raman spectrometer equipped with a Spectra-Physics 250 helium-neon laser for excitation at $5145\text{\AA}$ and $5689\text{\AA}$. The scattered radiation was detected at approximately 180° geometry with a thermoelectrically cooled S-20 photomultiplier tube and photon counting system. Samples were sealed in 4mm fused silica tubing.

Ultraviolet/Visible spectra. Absorption spectra in the UV/visible region reported in this research were obtained using a Cary Model 14 recording spectrophotometer. The technique of S. Brown (61) was used in order to obtain spectra of air-sensitive compounds. Cylindrical fused silica reaction vessels were used for such samples with 1.0 cm path length cells filled with water used in the reference beam.

X-Ray Powder Spectra. The powder spectra of all new compounds re-

ported in the work were obtained using an XRD-5 General Electric Camera. Samples were contained in 0.5 mm Lindemann glass capillaries which were loaded in the dry box. Nickel-filtered copper K α radiation was used with an exposure time varying between three and five hours.

Magnetic Susceptibility. Values for the magnetic susceptibility of the compounds reported in this work were obtained by the Gouy method. Measurements were made using an Alpha AL 7500 water-cooled magnet with 4 in. pole faces and 1.5 inch air gap at field strength of 5KG. The 4 mm OD sample tube was standardized with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. Diamagnetic corrections were applied using Pascal's constants.

Gas Chromatography. Identification of organic products involved in this work was facilitated through the use of a Hewlett-Packard Model 5750B gas chromatograph using a flame ionization detector. Solid support used in the six foot by 3/8 inch columns was Chromasorb W with a 10% QF-1 liquid phase. Nitrogen was used as the carrier gas. Oven temperature was typically between 100-180°C.*

Chemical Analysis. Standard analysis of new compounds reported in the work were performed by the Beller Microanalytical Laboratory in Göttingen, West Germany. Analyses of chromyl fluoride were performed by the author by condensing a sample in a fused silica vessel, hydrolysing the sample with boiled, distilled water, and diluting the solution in a volumetric flask. Hexavalent chromium was determined iodometrically, using standardized thiosulfate solution. Acidity was measured by titration with standard base using phenolphthalein indicator and reported as mmoles of acid. One mole of chromyl fluoride hydrolyses to yield four moles of pro-

* Unless otherwise stated, all temperatures reported in this thesis are in degrees Celsius.

tons in the form of two moles of HF and one mole of H_2CrO_4 .

Molecular Weight Determinations. Molecular weight determinations of vapors were accomplished by the vapor density method. A calibrated 100 ml Pyrex glass bulb fitted with an Eck and Krebs high vacuum Teflon stopcock was used as the sample vessel. Molecular weights are reported in g/mole.

Melting Points. Determination of melting points was accomplished through the use of a Mel-Temp apparatus equipped with a 400° thermometer.

Apparatus

Vacuum Lines. Vacuum lines used in this research consisted of either a metal or glass manifold evacuated through a liquid nitrogen-cooled trap by a Duo-Seal Model 1400 vacuum pump. Glass lines were constructed of 22 mm Pyrex glass tubing and fitted with Eck and Krebs 2 mm high vacuum stopcocks attached to outer 10/30 $\frac{3}{4}$ ground glass joints. A dual leg mercury manometer constructed of 10 mm Pyrex glass tubing was also attached to the manifold. Pressure below 1 mm Hg was estimated by a Televac thermocouple vacuum gauge with a typical working vacuum of 2 to 4×10^{-2} torr. The stopcocks were lubricated with Apiezon Type M grease while Dow Corning brand silicone grease was generally used on the ground glass joints.

The metal line used for the transfer of chromyl fluoride and chlorine monofluoride was constructed of 6 mm Monel tubing silver soldered with Monel connectors. VWR stainless-steel and Autoclave Engineering Space Saver valves were fitted to the line via Swagelock fittings. The surge vessel which comprised most of the line's 1.8l liters was made of copper. An Acco diaphragm type vacuum gauge was used to monitor vacuum from 1 mm to

760 mm while high vacuum was estimated with a Kontes thermocouple vacuum gauge. Typical working vacuum was 1 to 3×10^{-2} torr. Brass 10/30 $\frac{3}{8}$ outer joints allowed attachment of vessels to the line.

The metal line used for the transfer of tungsten and molybdenum hexafluoride was constructed of 6 mm copper tubing soldered to brass connectors. VWR stainless-steel valves were attached via Swagelock fittings as were the brass outer 10/30 $\frac{3}{8}$ joints. Vacuum was monitored through the use of a Televac thermocouple vacuum gauge.

Fluorine Line. Fluorine was dispensed in a $\frac{1}{4}$ inch OD brass line fitted with a Ni helice filled, -78 cooled brass U-trap. VWR valves were connected through the use of a Swagelock fittings as were the brass 10/30 $\frac{3}{8}$ outer joints. Pressure was monitored on an Acco dial vacuum/pressure gauge.

Reaction Vessels. Reaction vessels were composed of either Pyrex glass, fused silica, stainless-steel, or Monel. The Pyrex glass vessels were constructed from a 100 ml round bottom flask to which had been sealed a Kontes high vacuum stopcock fitted with an inner 10/30 $\frac{3}{8}$ ground glass joint. The fused silica vessels were similarly outfitted but the body of the vessel was cylindrical, being constructed of 22, 40, or 54 mm tubing resulting in a vessel volume of 30, 100, or 250 ml, respectively. The body of the vessel was attached to the stopcock through a graded seal. The Pyrex glass and fused silica vessels were equipped with Teflon coated stirring bars.

The two sizes of stainless-steel vessels were of a 35 mm diameter and had a volume of approximately 100 or 200 ml. These vessels were equipped with either Hoke or VWR valves attached to metal 10/30 $\frac{3}{8}$ inner joints. The Monel reaction vessel was fitted with an Autoclave Engineering Space

Saver valve attached to an inner 10/30 $\frac{1}{8}$ joint. The metal vessels were passivated by heating with the particular fluorinating agent before reactions were run. Frequently nickel metal shot (2 mm diameter) was added to the vessels to facilitate mixing of reactants.

Dry Box. Handling of all air-sensitive reagents and products was done in a KSE dry box. Nitrogen used as the atmosphere in the box was dried by passing it through a column packed with phosphorous pentoxide and calcium chloride. Maintenance of a dry environment in the box was accomplished with an exposed container of phosphorous pentoxide left in the chamber.

Chromyl Fluoride Addition Vessel. The chromyl fluoride addition vessel was constructed of 52 mm Pyrex glass tubing and fitted with one Kontes high vacuum stopcock and one Eck and Krebs vacuum stopcock. The volume of the vessel was approximately 500 ml. The vessel, as used, is illustrated in Figure 1.

Vacuum Traps. Vacuum traps were constructed of 22 mm tubing and fitted with a concentric 10 mm inner tube. Kontes high vacuum stopcocks were fitted and 10/30 $\frac{1}{8}$ ground glass joints allowed attachment to the vacuum line and to other vessels.

Reagents

Chromium Trioxide. Chromium trioxide (Mallinkrodt, Reagent Grade) - CrO_3 was dried for 24 hours in a 110° oven and stored in a glass container in the dry box. The compound was transferred to the reaction vessel in the dry box before use.

Chlorine Monofluoride. Chlorine monofluoride (Ozark-Mahoning) - ClF was transferred from the commercial storage cylinder in a metal vacuum line described elsewhere. No purification was attempted. Infrared spectra agree with the literature (42) with no extraneous absorbances noted.

FIGURE 1
Chromyl Fluoride Etard Reaction Apparatus

Chromyl Fluoride. CrO_2F_2 used in this research was prepared by the methods described in Chapter II. Chromyl fluoride was stored over NaF in a stainless-steel vessel which was attached to a metal vacuum line described elsewhere. Before use, the CrO_2F_2 was cooled to -78° and subjected to a dynamic vacuum to remove any residual HF or other volatile materials. The compound was then transferred to the reaction vessel via vacuum distillation in the metal vacuum line.

Sodium Fluoride. Sodium fluoride (Mallinkrodt, Reagent Grade) - NaF was fused in a nickel crucible and allowed to cool in the dry box where it was transferred to the vessel of interest.

Chromyl Chloride. Chromyl chloride (Alfa-Inorganics) - CrO_2Cl_2 was vacuum distilled from a vessel containing metallic mercury (to absorb residual Cl_2) and condensed at -196° .

Fluorine. Fluorine (Air Products, 98%) - F_2 was passed through a Ni helice filled, -78° cooled trap before condensation at -196° on a metal line described elsewhere.

Tungsten Hexafluoride. Tungsten Hexafluoride (Ozark-Mahoning) - WF_6 was purified by first condensing a sample over NaF and then subjecting it to a dynamic vacuum at -78° . The purified WF_6 was stored over NaF in a glass container at room temperature before vacuum distillation at -78° into a reaction vessel.

Molybdenum Hexafluoride. Molybdenum hexafluoride - MoF_6 was prepared using the method of Pitts and Jache (20). Powdered molybdenum (MCB, 99.9%) was treated with excess ClF and allowed to stand at room temperature for 12 hours. Residual chlorine and ClF were removed at -78° resulting in pure MoF_6 . The infrared spectrum agreed with the literature (62). The compound was handled in the same manner as WF_6 .

Sulfur Hexafluoride. Sulfur hexafluoride (Matheson, 99.8%) - SF_6 was used as received. The infrared spectrum agreed with the literature (63).

Nitryl Fluoride. Nitryl fluoride (Ozark-Mahoning) - NO_2F was vacuum distilled onto NaF contained in a metal vessel and then transferred at -78° to the reaction vessel. The infrared spectrum agreed with the literature (64).

Nitrosyl Fluoride. Nitrosyl fluoride (PCR) - NOF was purified in a manner similar to NO_2F ; however, due to the fact that it was very impure, (NO_2 and HF were the major impurities) only repeated -78° distillations over NaF resulted in a pure starting material. The infrared spectrum agreed with the literature (64).

Carbonyl Fluoride. Carbonyl fluoride (PCR) - COF_2 was condensed over NaF at -196° and then vacuum distilled into the reaction vessel. The infrared spectrum agreed with the literature (63).

Antimony Pentafluoride. Antimony pentafluoride (PCR) - SbF_5 was purified by condensing over NaF and subjecting it to a dynamic vacuum at 0° . Every effort was made to completely degas the compound before vacuum distillation into the reaction vessel.

Freon-113. Freon-113 (Matheson) - 1,2,2 trichloro-1,1,2-trifluoroethane was dried over P_4O_{10} and vacuum distilled.

Tetrachloroethylene. Tetrachloroethylene (B & A, Reagent Grade) - $\text{Cl}_2\text{C}:\text{CCl}_2$ was dried over P_4O_{10} and vacuum distilled.

1,1-Difluoroethylene. 1,1-Difluoroethylene (PCR) - $\text{F}_2\text{C}:\text{CH}_2$ was used as received. The infrared spectrum agreed with the literature (63).

Trifluoroethylene. Trifluoroethylene (PCR) - $\text{F}_2\text{C}:\text{CHF}$ was used as received. The infrared spectrum agreed with the literature (63).

Molecular Sieves. Molecular sieves (Linde Type 4A, MCB) - were used as received for final drying of organic solvents.

All other common reagents used were of the highest purity available.

CHAPTER II

NEW PREPARATIONS OF CHROMYL FLUORIDE

Introduction

Chromium dioxide difluoride (chromyl fluoride) was first reported 148 years ago when German chemists noted the red vapors of what was found to be a chromium fluoride above a hot solution of fluorspar, chromates, and sulfuric acid (1). The positive identity of the compound was not known for some time although it was thought to be chromium hexafluoride (2). Fredenhagen (3) isolated a red-brown, easily condensable gas from the reaction between anhydrous HF and alkali chromates and speculated that it might be CrO_2F_2 but he did not attempt to isolate the compound. In 1941, v. Wartenberg (4) synthesized impure CrO_2F_2 by treating chromyl chloride with elemental fluorine and reported it to be a strong fluorinating agent, a conclusion which is incorrect due to the fact that v. Wartenberg's chromyl fluoride was contaminated with free F_2 (reaction with water yielded ozone). Engelbrecht and Grosse (5) were the first to prepare pure chromyl fluoride, using anhydrous HF and CrO_3 , and collected physical chemical data which are listed in Table I.

The recent literature contains numerous methods of preparing chromyl fluoride. These techniques most always involve the use of moderate to strong fluorinating agents and either chromium trioxide or chromyl chloride. A list of these preparations is found in Table II. Many of these methods suffer from problems in purifications of the product, in unwanted side reactions, or in requiring the use of elemental fluorine.

TABLE I
PHYSICAL PROPERTIES OF CHROMYL FLUORIDE

Melting Point	31.6 °	
Quasi Boiling Point	29.6°*	
ΔH_{fus} (kcal/mol)	5.6	*Temperature at which vapor pressure equals 760 mm.
ΔH_{sub} (kcal/mol)	13.8	
ΔH_{vap} (kcal/mol)	8.2	

TABLE II
PREVIOUSLY REPORTED PREPARATIONS OF CHROMYL FLUORIDE

		REF
II-A	$CrO_3 + 2HF \xrightarrow{25^\circ} CrO_2F_2 + H_2O$	5
II-B	$CrO_2Cl_2 + F_2 \xrightarrow{200^\circ} CrO_2F_2 + Cl_2$	4
II-C	$CrO_3 + F_2 \xrightarrow{150^\circ} CrO_2F_2 + \frac{1}{2}O_2$	6
II-D	$CrO_3 + SF_4 \xrightarrow{5^\circ} CrO_2F_2 + SOF_2(+SO_2)$	7
II-E	$CrO_3 + 2CoF_3 \xrightarrow{200-300^\circ} CrO_2F_2 + 2CoF_2 + \frac{1}{2}O_2$	8
II-F	$CrO_3 + IF_5 \xrightarrow{100^\circ} CrO_2F_2 + 10F_3$	9

Prior to the new methods of CrO_2F_2 synthesis described in the following paragraphs, this laboratory used the method of Flesch and Svec (8), involving the reaction of cobalt trifluoride and chromium trioxide at temperatures up to 300° ; to prepare chromyl fluoride. This technique is useful for making small quantities (less than five grams) but it is not practical for preparation of large quantities of CrO_2F_2 . In the metal flow system that is used, chromyl fluoride can easily solidify to block the flow, causing serious problems in keeping the moisture-sensitive product pure. The blockage is most likely to occur from 200 - 300° , once the chromium trioxide melts and the reaction is most vigorous.

Due to the fact that relatively large quantities of CrO_2F_2 were needed for the study of its reaction chemistry, new preparative routes to chromyl fluoride were sought. A total of five new synthesis methods were found; among them are the most convenient and least expensive preparations thus far reported. These are listed in Table III.

TABLE III

NEW PREPARATIONS OF CHROMYL FLUORIDE

Reaction Chemistry of Fluorinating Agents Used in the Preparation of Chromyl Fluoride

As a fluorinating agent, chlorine monofluoride has been assigned to be relatively less reactive than F_2 , ClF_3 , BrF_5 , and IF_7 (10,11);

however, ClF has found moderate use in preparative inorganic chemistry. It has been shown to react with perfluorinated ketones and alcohols to form perfluorinated hypochlorites (12):

R_f = perfluorinated alkyl group

Sulfur trioxide reacts with ClF to form chlorine fluorosulfate (13):

Chloryl fluoride can be prepared from oxygen and ClF (14):

In studying the complex reaction of excess ClF_3 and UO_2F_2 , three groups (15,16,17) concur that the overall reaction is:

However, in side reactions where chlorine monofluoride is produced such as in equation II-6, ClF can also act as a fluorinating agent as shown in equation II-7.

Shrewsberry and Williamson (16) also studied the reaction of ClF and UO_2F_2 and found it to be slower than the corresponding reaction of ClF_3 . It was discovered that chloryl fluoride was also a product of the reaction of both ClF and ClF_3 with UO_2F_2 . This lessened the amount of oxygen and chlorine obtained as well as reducing the effectiveness of the fluorinating agent since a fluorine appears in something other than the intended product.

It was assumed that equation II-8 described the reaction producing ClO_2F from chlorine monofluoride and uranyl fluoride and that the actual situation was a combination of equations II-7 and II-8 since Cl_2 , O_2 , ClO_2F ,

and UF_6 were all found to be products of the reaction. The oxygen and chlorine were proposed to have come from the thermal decomposition of chloryl fluoride (18) which is described by the reverse of equation II-4. It appears that there is a high temperature equilibrium between oxygen, chlorine monofluoride, and chloryl fluoride. Ellis and Forrest (15) also found ClO_2 and Cl_2O as products of the reaction but these were attributed to wet apparatus by Luce and Hartmanshenn (17). It has since been shown that chloryl fluoride will react with UF_4 and UF_5 to form ClO_2 and UF_6 (19) which would account for the presence of the chlorine dioxide.

Pitts and Jache (20) studied the reactions of ClF with some Group VI elements and compounds. The important reactions are listed in equations II-9 through II-14.

In reaction II-14, chloryl fluoride was also found among the volatile products of the reaction although no attempt was made to quantify the amount or to explain the mechanism of its origin.

The above mentioned work has recently been complimented with more study of the reactions between Group VIa compounds and chlorine monofluor-

ide (21). It was found that sulfur and selenium tetrachloride react with ClF at room temperature to form chlorine and SF_4 and SeF_4 , respectively. Selenium dioxide, when treated with chlorine monofluoride, gave oxygen, chlorine, chlorine dioxide, and chloryl fluoride as well as $SeOF_2$. Excess ClF produced SeF_4 from SeO_2 while SeF_6 and SeF_5Cl were formed from $SeOF_2$ with similar side products. Analogous reactions have been observed for tellurium compounds (22).

It has been shown that BrF_5 , BrF_3 , and ClF_3 react with chromium trioxide at or below room temperature to give chromium (V) oxyfluoride adducts of the fluorinating agents with the production of only a small amount of chromyl fluoride (23, 24, 25). These reactions will be discussed in Chapter IV of this thesis.

The reaction chemistry of the hexafluorides of tungsten and molybdenum has not been widely studied. O'Donnell and Stewart (26) have investigated the relative reactivity of MoF_6 and WF_6 as outlined in Table IV.

TABLE IV

REACTIONS OF MOLYBDENUM AND TUNGSTEN HEXAFLUORIDES

MoF_6 and WF_6 was found not to react with AsF_3 , BiF_3 , or SbF_3 . Molybdenum hexafluoride was found to be much more reactive than WF_6 in halogen-exchange involving PCl_3 , $AsCl_3$, $SbCl_3$, and others to produce fluorinated substrates and $Mo_2Cl_3F_6$. No examples of oxygen-halogen exchange reactions involving WF_6 nor MoF_6 could be found in the literature.

Fawcett has found carbonyl fluoride to be a novel fluorinating agent. The reaction of COF_2 with I_2O_5 proceeds at 200° to produce IF_5 (27):

Stannic fluoride can be prepared from tin(IV) oxide (28):

Carbonyl fluoride, in the presence of a nitrogenous base, will fluorinate carbonyl groups, producing gem-difluorides, similar in reactivity to sulfur tetrafluoride (29). In the absence of base, fluorinated fluoroformates are produced. Similar transformations of carbonyl groups to produce chlorinated products have been reported using phosgene (30).

Chromyl chloride can be produced as a result of the reaction of hexavalent chromium with acid chlorides:

Sulfur hexafluoride has customarily been thought of as being relatively chemically inert; however, it has been shown that SF_6 is an active fluorinating agent at elevated temperatures. Opalovsky and Lobkov (33) studied the interaction of SF_6 with metals and metal oxides. From 500 - 600° it was found that metals, such as the alkaline earths and rare earths, reacted with SF_6 to form fluorides and sulphides. The oxides of the same metals formed fluorides with SF_6 at 600 - 700° . Sulfur trioxide reacts with SF_6 at 250° to form sulfuryl fluoride in 20% yield (34):

Recently, the thermal decomposition products of SF_6 in glass have been worked out (35). It has been reported that between 700 - 900° , the products

obtained are a result of reaction with the vessel. The equation proposed was:

Experimental

Reaction of Chlorine Monofluoride and Chromyl Chloride. To 31 mmoles CrO_2Cl_2 contained in a 100 ml stainless-steel reaction vessel was added 64 mmoles ClF at -196° . The reaction mixture was warmed to -78° and this temperature was maintained for 24 hours after which time the volatile products (at -78°) were removed. These vapors included the excess ClF and Cl_2 . The vessel was warmed to room temperature, then recooled to -78° and re-evacuated. A small amount of Cl_2 was evident in the trap. The vessel was warmed again to room temperature and the product (31 mmoles CrO_2F_2) was transferred to a storage vessel. The infrared spectrum of the product showed only CrO_2F_2 (41). Analysis: (Cr^{+6} ; Requires: 42.62% Found: 42.7% Acidity; Requires: 12.10 mmoles Found: 12.23 mmoles).

Reaction of Chromium Trioxide and Chlorine Monofluoride at 0°C .

Dried CrO_3 (45 mmoles) was added to a 100 ml stainless-steel reaction vessel in the dry box followed by the addition of 94 mmoles ClF at -196° via vacuum distillation. The reaction was then placed in 0° bath for approximately 12 hours after which time the vessel was evacuated at -196° . The only volatile product at this temperature was found to be O_2 , identified by its molecular weight (Requires: 32.0, Found: 32.1). At -78° the volatile products were ClF and ClO_2F , as identified by their characteristic infrared absorbances (See Table VI) and Cl_2 , identified by its molecular weight (Requires: 71.0 Found: 74.8, Note: Infrared spectrum of the molecular weight sample showed a small amount of SiF_4 to be present) and its approximately 100 mm liquid vapor pressure at -78° . At room temperature the only volatile product was CrO_2F_2 , identified by its infrared

spectrum (41). The yield of CrO_2F_2 was 45 mmoles or 100% based on CrO_3 . Analysis (Cr^{+6} ; Requires: 42.62% Found: 42.43%, Acidity; Requires: 6.364 mmoles Found: 6.304 mmoles).

Following a procedure similar to the above-outlined method, 25 mmoles of CrO_3 and 24 mmoles of ClF were brought to 0° in a stainless-steel reaction vessel. Upon evacuation of the vessel at -196° , oxygen was removed. At -78° , an infrared spectrum of the volatile products was taken in an all-metal vacuum line. The spectrum showed no ClF , only ClO_2 (See Table VI). At room temperature the only volatile product was CrO_2F_2 (24 mmoles).

Reaction of Carbonyl Fluoride and Chromium trioxide. To a 100 ml stainless-steel reaction vessel equipped with a Hoke valve was added 9 mmoles of dried CrO_3 in the dry box. Carbonyl fluoride (24 mmoles) previously condensed over NaF , was transferred into the vessel via vacuum distillation and the reaction mixture was heated to 185° for 12 hours in a tube furnace. Upon cooling the vessel to -78° and opening it to an evacuated -196° trap, white bands formed immediately in the liquid nitrogen-cooled receiver. The trap contents were shown to be COF_2 and CO_2 by infrared analysis. The room temperature volatiles consisted solely of CrO_2F_2 as shown by its infrared spectrum (41). The yield of chromyl fluoride was 100% based on chromium trioxide. Analysis (Cr^{+6} ; Requires: 42.62% Found: 42.71%, Acidity; Requires: 4.157 mmoles Found: 4.145 mmoles).

In another preparation, using the above-outlined procedure, 12 mmoles of dried CrO_3 and 9 mmoles of COF_2 were added to a reaction vessel and heated as above. When the vessel was evacuated at -78° , the only volatile product observed in the infrared spectrum was CO_2 . A molecular weight

determination was performed on the -78° volatile product: (Requires 44.0 g/m, Found 43.9 g/m). After evacuation at room temperature which removed the product, CrO_2F_2 , the vessel was found to contain 3 mmoles of unreacted CrO_3 .

Reaction of Tungsten Hexafluoride with Chromium Trioxide. To a 200 ml stainless-steel vessel equipped with a VWR valve was added 28 mmoles dried CrO_3 in the dry box. The vessel was then evacuated and 23 mmoles of WF_6 was transferred at -78° via vacuum distillation. The reaction was heated to 125° for 12 hours, after which time the vessel was attached to a vacuum line and the volatile product investigated. Upon opening the vessel to the vacuum line at room temperature, the only volatile material remaining in the vessel was found to be CrO_2F_2 , as identified by its infrared spectrum (41) and subsequent analysis: (Cr^{+6} ; Requires: 42.62% Found 41.95%, Acidity; Requires: 9.23 mmoles Found: 9.31 mmoles). The yield was 100% based on WF_6 .

In another run, 10.55 mmoles of dried CrO_3 was placed in a 30 ml fused silica reactor. The vessel was evacuated and 75.78 mmoles of WF_6 was transferred via vacuum distillation at -78° . The reaction mixture was then warmed to 45° where after one hour red-brown vapors appeared above the liquid WF_6 . The reaction was allowed to stir overnight. When evacuated the only volatile materials indicated in the infrared spectrum were CrO_2F_2 , WF_6 , and SiF_4 leaving behind a grey-white solid. More dried WF_6 was added to the vessel and the solution set to stir for two additional hours at 60° . Red-brown vapors became evident immediately upon heating. The vessel was re-evacuated, leaving an off-white powder. The powder was sublimed and the white crystalline sublimate was found to melt from 102 – 104° . WOF_4 has a reported melting point of 105° (39). Analysis: W(Requires: 66.64% Found: 66.75%) F(Requires: 27.5% Found: 27.7%).

Reaction of Molybdenum Hexafluoride and Chromium Trioxide. To 24 mmols of CrO_3 contained in a 200 ml stainless-steel vessel fitted with a VWR valve was added 11 mmols of MoF_6 at -78° via vacuum distillation. The reaction vessel was heated to 125° for 12 hours and then evacuated at room temperature. The only volatile product was found by infrared analysis to be chromyl fluoride (41). The weight loss indicated that the total CrO_2F_2 produced was 1.4 g (11 mmols). Analysis (Cr^{+6} ; Requires: 42.62% Found 42.51%, Acidity; Requires: 6.010 mmols found: 5.915 mmols). Sublimation of the nonvolatile residue yielded a white solid which had a melting point of $95-97^\circ$. The reported melting point of MoOF_4 is 97° (40). Analysis (Mo; Requires: 40.4% Found: 40.0%, F; Requires 51.0% Found: 51.0%). The yield was 100% based on MoF_6 .

In another reaction, 23.57 mmols of CrO_3 was placed in a 30 ml fused silica reaction vessel. The vessel was evacuated and 9.623 mmols of MoF_6 was vacuum distilled into the vessel at -78° . The reaction mixture was allowed to warm to room temperature and reddish-brown vapors were evident immediately upon the melting of the MoF_6 . The reaction was allowed to stir for two hours at room temperature (22) and the reddish-brown color of the vapors became increasingly intense. The vessel was evacuated at room temperature and chromyl fluoride and silicon tetrafluoride were the only volatile components to be observed in the infrared spectrum.

Reaction of Chromium Trioxide and Sulfur Hexafluoride. To 27 mmols of CrO_3 contained in a 200 ml stainless-steel reaction vessel equipped with a VWR valve was added 35 mmols of SF_6 at -196° . The reaction mixture was heated to 185° for 24 hours after which time the vessel was evacuated at -78° . The infrared spectrum of the -78° volatiles showed only SF_6 . There

were no products volatile at room temperature. The reaction vessel was found to contain only unreacted CrO_3 .

A similar reaction was run at 330° . No chromyl fluoride was obtained.

Discussion

Reaction of CrO_2Cl_2 and ClF

The reactivity of chlorine monofluoride can be best explained if one assumes the compound to be chlorine(I) fluoride, implying that the chlorine is on the positive end of a very polarized bond. In the reaction of ClF with CrO_2Cl_2 there is a simple halogen exchange, forming CrO_2F_2 , while the chlorine fragments, chloride and unipositive chlorine form molecular chlorine analogous to the SeCl_4 reaction with ClF already mentioned. The balanced equation is given below:

Reaction of CrO_3 and ClF

In the CrO_3 reaction with ClF the situation is not so simple. It has been shown, as was mentioned earlier, that ClF will add across a double bond to oxygen with the product having Fluorine bonded to the central atom and the chlorine attached to oxygen in a hypochlorite structure. Examples of this behavior are the reactions of SO_3 (13) and perfluorinated ketones and alcohols (12). In addition, ClF can also fluorinate oxides to form non-chlorine containing products. Examples of this sort of reactivity include the reactions of chlorine monofluoride with selenium dioxide, tellurium dioxide, tungsten trioxide, and uranyl fluoride.

In all of the latter reactions chloryl fluoride (ClO_2F) has been reported as a product of the reaction. Christie (36) has shown that chlorine dioxide reacts with chlorine monofluoride to give chloryl fluoride and chlorine.

This reaction has been assumed by others (21). A reasonable mechanism can be assigned for the reaction of ClF and CrO_3 assuming chlorine monoxide to be the original co-product of the reaction. This is presented in Figure 2. The first step in the proposed mechanism involves addition of ClF across a chromium-oxygen double bond to form a hypochlorite intermediate which reacts with a second molecule of chlorine monofluoride to form chlorine monoxide and chloryl fluoride which separates from the CrO_3 polymer. Cl_2O would not survive long enough to be detected in the presence of ClF and would be converted to ClO_2F and Cl_2 .

Chloryl fluoride may also be formed as a result of the reaction of ClF with glass or with unpassivated metal surfaces (20) (ClO_2 is also reported as a product). Chlorine monofluoride will react with small amounts of water to produce ClO_2F (36). In addition, chloryl fluoride and chlorine are the products of the reaction of ClF and ClO_2 (36). It becomes clear that ClO_2F is the most prevalent chlorine oxide to be found in the presence of oxides and excess chlorine monofluoride (or chlorine trifluoride) so that it seems reasonable to assume that ClO_2F may not be a direct product of the reactions involving ClF and oxides. It is assumed that the ClO_2F obtained in the reaction of CrO_3 and ClF is not the product of hydrolysis or glass attack since anhydrous conditions were maintained throughout, and in addition, working in an all metal system still allowed the detection of chloryl fluoride.

This above-outlined assertion and the accompanying mechanism are strengthened by the fact that in a reaction of ClF and TeO_2 where excess tellurium dioxide was used, chloryl fluoride was not observed but rather chlorine dioxide (21). In addition, in this research when excess chromium

Figure 2. Proposed Mechanism of the Reaction of Chlorine Monofluoride and Chromium Trioxide at 0°

Figure 3. Proposed Mechanism of the Reaction of Chromium Trioxide and Carbonyl Fluoride

trioxide was treated with chlorine monofluoride at 0°, only ClO₂ was noted as a volatile product in addition to CrO₂F₂, Cl₂, and O₂. It has been reported (19) that chloryl fluoride can act as a fluorinating agent, giving UF₅ or UF₆ and ClO₂ from UF₄. Chloryl fluoride may also react with chromium trioxide to give ClO₂ and CrO₂F₂ which would account for the presence of chlorine dioxide in the reaction where excess CrO₃ was used.

The oxygen found as a product of the reaction can be explained in keeping with the proposed mechanism by taking into account that these chlorine oxides slowly decompose into their constituent elements slightly above room temperature. A study of the explosive decomposition of chlorine dioxide revealed that the reaction is hastened as the pressure is increased (37). The pressure inside the reaction vessels is on the order of 10 atmospheres which would seem to be enough to at least partially decompose any chlorine dioxide that might form. Additionally, there is the possibility that chloryl fluoride may also undergo a pressure-induced decomposition to oxygen and chlorine monofluoride, analagous to its thermal decomposition. This, however, is not documented in the literature.

In summary, the proposed explanation of the observed products are listed in Table V. A balanced overall reaction would be:

This preparation is very useful since the product chromyl fluoride can be easily freed of all other products of the reaction by simply subjecting the vessel to a dynamic vacuum at -78°. As much as fifteen grams of chromyl fluoride has been prepared using this method.

Reaction of CrO₃ and COF₂

The reaction of carbonyl fluoride and chromium trioxide goes quickly to completion to form chromyl fluoride and carbon dioxide. As was noted in the introduction, Fawcett found that COF₂ would add across double bonds

to carbon as though the compound was COF^+F^- , forming a fluorinated fluoroformate with carbonyl groups, for example. Assuming a mechanism similar to the one proposed for ClF and CrO_3 , a reasonable mode of reactivity is outlined in Figure 3.

TABLE V

PROPOSED EXPLANATION OF THE REACTION OF CHROMIUM TRIOXIDE
AND CHLORINE MONOFLUORIDE AT 0°C

The fluoroformate intermediate would rapidly attack the chromium to form chromyl fluoride and carbon dioxide. This mechanism is analagous to the one proposed for the reaction of SF_4 with carbonyl groups (38). This reactivity implies a decided nucleophilic character for the fluorine atoms of COF_2 similar to the behavior of the chlorines of phosgene and acid chlorides (30, 31, 32).

Reaction of CrO_3 and SF_6 , MoF_6 , and WF_6

The reaction of molybdenum hexafluoride and tungsten hexafluoride with chromium trioxide proceeds at a moderate temperature to form chromyl fluoride while sulfur hexafluoride does not react even at elevated temperatures, above the decomposition temperature of chromium trioxide. It seems probable that, in light of the previous work on SF_6 , chromyl fluoride could be formed at perhaps even higher temperatures (up to 450°, the decomposition point of CrO_2F_2) but this sort of synthesis would not be practical nor would it give high yields due to the decomposition of chromium

TABLE VI
 INFRARED ABSORBANCES (in cm^{-1}) OF VOLATILE PRODUCTS
 OF THE REACTION OF CrO_3 AND ClF AT 0°

<u>xs ClF and CrO_3</u>	<u>xs CrO_3 and ClF</u>	<u>ClF (42)</u>	<u>ClO_2F (43)</u>	<u>ClO_2 (44)</u>
1276, 1265 (s)			1280, 1265 (s)	
1115, 1105, 1090 (m)	1120, 1105, 1092 (s)		1120, 1106, 1095 (m)	1121, 1110, 1095 (s)
	960, 940 (m)			957, 935 (m)
790, 770, 750 (m)		792, 785, 765, 750 (s)		
640, 625, 615 (m)			625, 620, 615 (m)	
560, 545, 530 (m)			555, 540, 525 (m)	

trioxide at far lower temperatures.

The production of chromyl fluoride from the hexafluorides of molybdenum and tungsten and chromium trioxide provides the simplest and most convenient route to CrO_2F_2 thus discovered. The reaction will occur only slowly at room temperature, but elevated temperatures hasten the process and drive the reaction to completion. An added feature of these reactions is that the use of a high pressure vessel is not required and small quantities can even be produced in a very dry fused silica vessel. Since the reactants consist of a nonvolatile reagent (CrO_3) and a volatile fluorinating agent (MoF_6 , WF_6) which form a volatile and nonvolatile product, CrO_2F_2 and MoOF_4 or WOF_4 , respectively; purification is greatly simplified. In addition, this provides a straightforward synthesis of the oxide tetrafluorides of molybdenum and tungsten, which can be obtained pure via sublimation.

In line with the reported relative reactivities of the two hexafluorides (26), MoF_6 produced chromyl fluoride more readily than did WF_6 ; the former at room temperature while the latter only conveniently when heated to at least 45° . Higher temperatures were used in the bulk synthesis of CrO_2F_2 to insure complete reaction.

Conclusion

Chlorine monofluoride, carbonyl fluoride, tungsten hexafluoride, and molybdenum hexafluoride have all been shown to be useful in the preparation of chromyl fluoride. These reactions proceed to completion with little or no problem in purification of the product. An interesting factor concerning these reactions is the relative cost involved in the starting materials. The above mentioned methods are the least expensive ways of making CrO_2F_2 , particularly those involving WF_6 and MoF_6 .

The reaction of chromyl chloride and chlorine monofluoride is straight forward, but the other preparations are preferred due to the possibility of forming chromyl chloride fluoride (CrO_2ClF) as a contaminant unless one is certain excess ClF is used.

The mechanisms proposed for the reactions of carbonyl fluoride and chlorine monofluoride with chromium trioxide are based solely on the previously reported reactivity of these reagents as well as attempts to explain the formation of products observed. Unfortunately, there was no way to verify the mechanism through the use of a mass balance of components. Teflon packed gas chromatographs have been used in similar work with chlorine fluoride reaction studies (16) and one would have been useful here to quantify the product concentrations.

No mechanism was proposed for the reactions of WF_6 and MoF_6 with CrO_3 but it seems likely these involve an oxygen and/or fluorine bridged chromium-tungsten or molybdenum species as an intermediate. In principle, these might be monitored using the characteristic infrared absorbances of these bridging modes since these absorbances have been relatively well characterized due to the ubiquity of fluorine and oxygen bridging in solid metal oxide fluorides.

CHAPTER III

SOME REACTION CHEMISTRY OF CHROMYL FLUORIDE

Introduction

Prior to the work done with CrO_2F_2 in this laboratory, rather little was known of its reactivity, with most of the literature concerned with the more widely known analogue, chromyl chloride. It was reported that chromyl fluoride reacts with arsenic trioxide, forming chromium trioxide and arsenic fluorides as well as producing BF_3 from boric oxide and SiF_4 from glass (45). Engelbrecht and Grosse (5) found that methane and butane were ignited at elevated temperatures by CrO_2F_2 , but KF and NaF did not combine with chromyl fluoride at room temperature. Chromyl chloride was found to undergo a halogen exchange with CrO_2F_2 to form CrO_2ClF (8). These studies represent the total reported work on chromyl fluoride to be found in the modern, pre-1960 literature.

More recent studies proved chromyl fluoride to have a greater thermal stability than chromyl chloride:

In addition, it is interesting to note that chromyl chloride undergoes photodecomposition readily to chromium dioxide and chlorine (46) while chromyl fluoride polymerizes under UV radiation with loss of oxygen (47).

The molecular structure of CrO_2F_2 has recently been reported as a result of an electron diffraction study (48). It was found that the

O=Cr=O bond angle was less than the F-Cr-F angle, which is just the opposite of an analogous compound, SO_2F_2 . It was proposed that ligand-ligand interactions are more important than electron-pair repulsions in determining the stereochemistry of CrO_2F_2 . Results of the study are listed in Table VII

TABLE VII
BOND LENGTHS AND ANGLES OF CHROMYL FLUORIDE

Cr=O	1.579Å
Cr-F	1.739Å
< O=Cr=O	102.14°
< F-Cr-F	118.91°

The infrared spectrum of CrO_2F_2 vapor has been recorded and assigned on the basis of C_{2v} symmetry (41). An infrared and Raman study of solid and liquid chromyl fluoride published recently from this laboratory (49) has shown the compound to be a polymer of cis-fluorine bridged tetrahedra, in accordance with an x-ray study (50).

A recent publication (51) contains most of what is known of the reaction chemistry of chromyl fluoride. It was found that CrO_2F_2 reacts with the Lewis acids SO_3 , TaF_5 , SbF_5 , and $(\text{CF}_3\text{CO})_2\text{O}$ to form the chromyl compounds, $\text{CrO}_2(\text{SO}_3\text{F})_2$, $\text{CrO}_2\text{F}(\text{TaF}_6)$, $\text{CrO}_2\text{F}(\text{SbF}_6)$, $\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})$, and $\text{CrO}_2(\text{CF}_3\text{COO})_2$, respectively. Nitric oxide, nitrogen dioxide, and sulfur dioxide react to produce the so-called inorganic Etard complexes, $\text{NO}\cdot\text{CrO}_2\text{F}_2$, $2\text{NO}_2\cdot\text{CrO}_2\text{F}_2$, and $\text{SO}_2\cdot 2\text{CrO}_2\text{F}_2$ which were shown to contain chromium in either a tetra- or pentavalent oxidation state depending on the complex. Of particular interest is the discovery that CrO_2F_2 reacts with alkali and alkaline earth fluorides to give fluorochromates:

The infrared spectra of the compounds was assigned assuming an octahedral, cis-dioxo configuration about the chromium center. This is the first example of an octahedrally coordinated hexavalent chromium atom. In another study (52) it was shown that chromyl nitrate, $\text{CrO}_2(\text{NO}_3)_2$ can be prepared from CrO_2F_2 and NaNO_3 .

The previous work on the reaction chemistry of chromyl fluoride with inorganic reagents has been augmented in this thesis by the preparation of nitronium and nitrosonium trifluorochromate(VI) salts synthesized by the reaction of NO_2F and NOF , respectively, with CrO_2F_2 . In addition, a 1:2 adduct was isolated from the inorganic Etard product, $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$, and acetonitrile. This product is analagous to those found to form between various solvents acting as Lewis bases and organic chromyl chloride Etard products (53).

The most widely known use of a chromyl compound has been in the oxidation of organic compounds; a process which has come to be called the Etard reaction. Alexander Leon Etard found in 1877 that a mixture of toluene and chromyl chloride dissolved in an inert solvent such as carbon tetrachloride or carbon disulfide produced an amorphous, hygroscopic, brown material which was insoluble in most common solvents. When this solid, the Etard product, was hydrolysed and the solution extracted, benzaldehyde could be isolated. Etard studied the reaction of chromyl chloride with a number of other organic compounds (54) but for the most part, this work has not been repeated.

In general, the Etard reaction involves the reaction of chromyl chloride with an alkane, an alkene, or an alkyl aromatic compound to produce a solid of composition varying between one to three moles of CrO_2Cl_2 per mole of hydrocarbon, depending on the particular organic substrate. The insolubility of the Etard product as well as its amorphous nature has hampered work on the elucidation of its structure; however, an ESR study of the 1:2 complex of diphenylmethane and chromyl chloride was interpreted as showing the presence of two different kinds of chromium atoms; one diamagnetic (hexavalent) and the other diamagnetic and probably quadravalent (57). This work has since been challenged (58). In one of the few other studies done on the complex, Makhija and Stairs (53) found that Etard's original complex (1 toluene: 2 chromyl chloride) formed a 1:2 complex with donor solvents such as acetonitrile, pyridine, dioxane, and others. Their interpretation of magnetic susceptibilities taken of the original complex as well as the adducts suggest that both chromium atoms were in the tetravalent oxidation state. This work was in agreement with a magnetic susceptibility study done by Wheeler (58) on the same complex. The proposal that both chromium atoms are in the tetravalent oxidation state also is consistent with the structure of the toluene complex originally postulated by Etard:

In practice, hydrolysis of the complex is done in the presence of a reducing solution containing sulfur dioxide or sodium sulfite to prevent further oxidation of the organic product. The oxidized product is most generally a ketone or an aldehyde but alcohols are also isolated. Chlorohydrins have also been found as products in the hydrolysis of alkene chromyl chloride complexes. A limited table of organic substrates and their chromyl chloride oxidation products is found in Table VIII.

TABLE VIII
CHROMYL CHLORIDE OXIDATION PRODUCTS

<u>Reactant</u>	<u>Product</u>	<u>Ref.</u>
toluene	benzaldehyde	54
n-hexane	2-hexanone, 3-hexanone	54
2-methylpentane	2-methyl-3-pentanone	55
1-hexene	2-chloro-1-hexanol (33%), 1-chloro-2-hexanol (9%), 1-chloro-2-hexanone (5%), 2-chlorohexanal (2%) (Percentages are of the total organic material isolated.)	56
cyclohexane	cyclohexanone	55
methylcyclohexane	2-methylcyclohexanone, 2-chloro-2-methylcyclohexanone	55

The reaction is characterized by relatively low yields (Overall yields based on amounts of original organic starting material are almost never reported.) and many side reaction products from substrates of lower reactivity. Hobbs and Houston (55) found that alkanes with a tertiary carbon-hydrogen bond reacted much more quickly than did an alkane without this feature. The Etard product obtained from the tertiary C-H containing compounds were of composition $1\text{HC}:2\text{CrO}_2\text{Cl}_2$, while other alkanes

complexes were analyzed as intermediate composition between 1:2 and 1:4, perhaps indicating a mixture of products.

Khunyanis (59) has studied the reaction of chromyl chloride with various fluoroolefins and found the resulting products rather surprising. For example, vinylidene fluoride and CrO_2Cl_2 yielded monochloroacetic acid while trifluoroethylene reacted with chromyl chloride to give fluorochloroacetic acids. Trifluorochloroethylene also gave a mixture of chlorofluoroacetic acids. Perfluoropropylene and isobutylene reacted with chromyl chloride to give the acid fluorides of α -chloroperfluoropropionic acid and α -chloroperfluoroisobutyric acid, respectively. In this work, no attempt was made to isolate or characterize the intermediate product; in fact, in the latter two cases listed above it appears that there was a direct reaction, with no Etard product-like intermediate evident. No explanation for the odd reactivity was given.

In another study, chromyl fluoride formed in situ from chromium trioxide and hydrogen fluoride at -78° was allowed to react with vinylidene chloride and 1,1-difluoroethylene (70). The result of the reaction after hydrolysis was a hypofluorination of the starting materials, forming dichlorofluoroethanol and trifluoroethanol, respectively. Again no attempt was made to isolate or characterize the intermediate product. It appears that chromyl chloride reacts via a different mechanism than chromyl fluoride.

In this research, the reaction of chromyl fluoride and hexane, 1,1-difluoroethylene, trifluoroethylene, and tetrachloroethylene were studied,

All these organic substrates yield an Etard product and attempts were made to identify structural features from the infrared spectra of the compounds. For the hexane and 1,1-difluoroethylene products, hydrolysis was performed and attempts at isolation of the resulting products were made.

Experimental

Preparation of $\text{NO}_2\text{F} \cdot \text{CrO}_2\text{F}_2$. To 9.16 mmoles of CrO_2F_2 in a 250 ml fused silica reaction vessel was added 20.1 mmoles of purified NO_2F at -196° . No reaction was evident upon warming to -78° nor upon placement of the vessel in a 0° bath. The reaction was allowed to stand at 0° for ten hours at which time there was still no evidence of reaction; however, there were traces of glass attack. The reaction mixture was then placed in a 45° water bath and after fifteen minutes, a yellow solid formed. The vessel was removed from the water bath after two hours and evacuated at -78° into a -196° trap. Infrared analysis of the volatile products at this temperature revealed the presence of SiF_4 , NO_2 , and NO_2F . Upon evacuation at room temperature, no unreacted CrO_2F_2 was found in the reaction vessel. The weight pickup of NO_2F corresponded to 9.14 mmoles, making the apparent composition 1.00 $\text{NO}_2\text{F} \cdot 1.00 \text{CrO}_2\text{F}_2$. The product is a pale yellow, very hygroscopic solid which darkens rapidly in the presence of moisture and dissolved in water to give an orange-yellow solution. Analysis (Cr; Requires: 27.82% found: 28.54%, N; Requires: 7.49% Found: 7.22%, F; Requires: 30.50% found: 29.5%). The compound does not melt but decomposes above 130°C in a melting point capillary, giving off NO_2 . An x-ray powder spectrum revealed to the compound to be amorphous. Infrared data are found in Table IX. Note: all tables are found in the "Discussion" section.

Preparation of NOF·CrO₂F₂

To 12 mmoles of CrO₂F₂ contained in a 200 ml stainless steel reaction vessel was added 26 mmoles of purified NOF at -196° via vacuum distillation. The reaction was allowed to stand at room temperature (23) for approximately 36 hours after which time the volatile components of the mixture were removed. Infrared analysis showed the presence of NOF and a small amount of NO₂. No CrO₂F₂ was evident. The weight pick-up of NOF corresponded to 12 mmoles, giving the adduct an apparent composition of 1.0:1.0. The product is a greenish-yellow powder which dissolves in water to give a yellow solution. Analysis (Cr; Requires: 30.4% Found: 32.5%, N; Requires: 8.19% Found: 9.03%, F; Requires: 33.3% Found: 33.6%). The solid doesn't melt but decomposes in a melting point capillary above 100°C to give a grey-green solid and NO₂. An x-ray powder spectrum showed the compound to be amorphous. Infrared data are found in Table IX.

Reaction of SO₂·2CrO₂F₂ and Acetonitrile

To 1.43 mmoles of freshly prepared SO₂·2CrO₂F₂ (51) in a 100 ml Pyrex glass reaction vessel was added approximately 0.1 mole CH₃CN via vacuum distillation from P₄O₁₀. The mixture was allowed to stir for 24 hours without evidence of reaction followed by heating at 60° for 48 hours. During this time the reaction mixture took on a light green color. Upon evacuating the vessel at room temperature, a straw-colored solid precipitated which had a dry weight pickup of acetonitrile corresponding to 2.87 mmoles. Infrared analysis of the volatile products from the reaction showed only CH₃CN and no SO₂ or any other would-be decomposition product. Analysis for SO₂·2CrO₂F₂·2CH₃CN (Cr; Requires: 26.6%

Found: 26.9%, F; Requires: 19.5% Found: 19.1%, N; Requires:
7.2%, Found: 7.08% C; Requires: 12.3% Found: 12.3% H; Requires:
1.51% Found: 1.55%. An x-ray powder spectrum revealed the adduct
to be amorphous. Infrared data are found in Table X.

Reaction of n-hexane and Chromyl Fluoride in Fused Silica

To a 200 ml fused silica reaction vessel containing 38.9 mmoles of n-hexane and 70.7 mmoles of Freon-113 was added 23.2 mmoles chromyl fluoride at -196° . The reaction mixture was warmed to -78° and kept at that temperature for approximately one hour after which the reaction was allowed to stir at 0° for 24 hours. A brown solid was formed as soon as the liquids melted. Upon evacuation of the reaction vessel a small amount of unreacted CrO_2F_2 was removed and trapped at -196° along with excess n-hexane and F-113. An infrared spectrum of the volatile materials of the reaction showed nothing other than n-hexane and F-113. The weight of the product corresponded to an n-hexane weight pickup of 4.85 mmoles making the apparent composition of the complex 4.85 mmoles n-hexane to 23.2 mmoles CrO_2F_2 or 1.00:4.78. Analysis: $\text{C}_6\text{H}_{14} \cdot 4\text{CrO}_2\text{F}_2$ Requires; Cr: 36.2% F: 25.5%, C: 12.5%, H: 2.44%, $\text{C}_6\text{H}_{14} \cdot 3\text{CrO}_2\text{F}_2$ Requires; Cr: 34.5%, F: 25.2%, C: 15.9%, H: 3.09%. Found; Cr: 35.19%, F: 26.4%, C: 11.07%, H: 2.52%. The product is a hygroscopic very very fine brown powder which dissolves in water to give a yellow-green solution with a characteristic pungent odor. An x-ray powder spectrum showed the complex to be amorphous. Infrared data are found in Table XI.

Reaction of n-hexane and Chromyl Fluoride in Glass Apparatus

In a typical run, 9.1 g (74 mmoles) of CrO_2F_2 was transferred to the chromyl fluoride addition vessel (see Figure 2) via vacuum distillation at -78° . Immediately thereafter, Freon-113, dried over P_{40}_{10} ,

was drawn into the vessel using the vacuum of the addition vessel. It was then vented to atmospheric pressure through a calcium chloride/phosphorous pentoxide drying tube attached to the addition vessel. To a one liter three-neck flask was added 16.5 g (192 mmols) of n-hexane and 351 g (1.87 moles) of F-113. The flask was then fitted with a thermometer, a calcium chloride/phosphorous pentoxide drying tube, and a 3 adapter for attachment of the addition vessel. When these were in place, the n-hexane and F-113 solution was cooled to 0° with an ice bath. The solution of chromyl fluoride in F-113 was added over the course of approximately one half hour such that the temperature of the hexane-containing solution did not rise above 3°. Immediately after the CrO_2F_2 solution came in contact with the hexane, a reddish-brown precipitate formed. During the course of the reaction, significant glass attack was evident on the addition vessel and the three-neck flask. After addition of chromyl fluoride, the reaction mixture was then filtered on a Schlenck-type pressure filtering apparatus equipped with a glass frit. The filter apparatus was then attached to a vacuum trap cooled to -196° and evacuated, with the complex being completely freed of any volatile materials. The trap contents were analyzed by infrared spectroscopy and gas chromatography with both methods revealing n-hexane and F-113 to be the only volatile material from the complex. Similar analysis of the filtrate from the pressure filtering gave the same results. The dried complex (9.6 g) was then stored in the dry box until a large sample of the complex was prepared for hydrolysis.

Analysis: $\text{C}_6\text{H}_{14} \cdot 4\text{CrO}_2\text{F}_2$ Requires: Cr: 36.2%, F: 26.5%, C: 12.5%
 H: 2.44%, $\text{C}_6\text{H}_{14} \cdot 3\text{CrO}_2\text{F}_2$ Requires: Cr: 34.5%, F: 25.2%, C: 15.9%
 H: 3.09%; Found; Cr: 37.7%, F: 26.5%, C: 9.95%, H: 2.20%.

Hydrolysis of the n-hexane Etard Complex

To a 500 ml Pyrex glass three neck flask equipped with Teflon stir bar was added 130 ml of a freshly prepared saturated solution of Na_2SO_3 . The solution was acidified to pH 2 with concentrated H_2SO_4 and then cooled to 0° with an ice bath and set to stir. The n-hexane Etard complex (21.6 g), prepared in glass apparatus, was added slowly to the reducing solution such that the temperature did not rise above 5° . At this point the solution took on an intense, dark green color. Testing a small sample of the solution with H_2O_2 and extracting with ether yielded a negative test for Cr(VI). Stirring was continued overnight, after which ether was added and the solution vigorously extracted twice. Before the third extraction, NaCl was added to saturate the solution. The collected ether extracts, totaling 70 ml, were pre-dried over Na_2SO_4 for one hour, followed by a 12 hour drying period over Linde 4A molecular sieves.

The dried ether solution was subjected to fractional distillation on a Kontes adiabatic distilling column packed with glass helices. The only fraction obtained was from 34.0° to 35.0° (ethyl ether) leaving approximately 7 ml (4 g) of a yellow-brown liquid in the pot. The solution darkened as ether was removed down to the final 7 ml. A rancid, butterscotch-like odor was noted from the liquid in the flask. An infrared spectrum of the liquid showed major absorbances listed in Table XII. The sample was transferred to a short path, microdistillation apparatus and heated. Again, the only fraction distilling over was ether, collected at 34.0° while the pot residue grew more deeply colored and the presence of a precipitative coating on the inside of the flask became evident.

Heating was stopped without collecting a non-ether fraction. Gas chromatographic analysis of the pot residue showed the presence of ether and at least ten other compounds. Ether amounted to approximately 17% of the total sample. Among the ten components was found 2-hexanone, and/or 3-hexanone, and n-hexanoic acid as identified by comparison to authentic samples. The infrared spectrum of the hydrolysate is presented in Table XII.

The Reaction of Chromyl Fluoride and 1,1-Difluoroethylene

To a 200 ml fused silica vessel was added 46.22 mmoles of CrO_2F_2 , followed by 103 mmoles F-113 and 38 mmoles of 1,1-difluoroethylene at -196° . The reaction mixture was warmed to -78° and a chocolate brown solid became evident where CrO_2F_2 had come in contact with the olefin. After about 30 minutes the vessel was transferred to a 0° bath whereupon the solvent melted and the reaction went to completion within another 30 minutes of stirring as evidenced by the lack of CrO_2F_2 vapors in the vessel. The vessel was then cooled to -196° and evacuated. An infrared spectrum of the volatile product at this temperature showed absorbances characteristic of carbon monoxide. A molecular weight of this gas agreed with the identity assumed from the infrared spectrum (Requires: 28.0 g/m Found: 27.0 g/m). The weight loss showed that the amount of CO was less than 3.6 mmoles. The vessel was then warmed to -78° and evacuated into a -196° cooled trap. An infrared spectrum of the volatile materials showed $\text{CF}_2\text{:CH}_2$, CO_2 , COF_2 , and F-113. The vessel was then evacuated at room temperature into a -196° cooled trap until constant weight was obtained. The room temperature volatile products were F-113 and excess difluoroethylene. No chromyl fluoride was obtained.

The weight pickup of olefin was 22.39 mmoles making the product an adduct of composition 1:2.06. Analysis for $\text{CF}_2\text{:CH}_2 \cdot 2\text{CrO}_2\text{F}_2$: Cr; Requires: 33.8% Found: 36.38%, F; Requires: 37.0% Found: 35.4%, C; Requires: 7.79% Found: 6.72%, H; Requires: 0.65% Found: 0.73%.

The product is a brown powder which decomposed at 120° , giving off a colorless gas while the solid turned green. It is moderately hygroscopic; forming a black solid in moist air with a definite fluorocarbon odor above the solid. Hydrolysis in water gives a yellow-green solution. The magnetic susceptibility of the compound was found to be 3.73 Bohr Magnetons.

A total 7.8 g of the complex was prepared and then hydrolyzed using a procedure and conditions described for the hydrolysis of the n-hexane-chromyl fluoride Etard Complex. The solution was extracted with ether and dried first over Na_2SO_4 then over Linde 4A molecular sieves. Gas chromatographic analysis of the ether extract revealed the presence of only one compound. The compound in the ether extract was not trifluoroethanol as evidenced by the presence of two peaks resulting from a coinjection of the ether extract and an authentic sample of $\text{CF}_3\text{CH}_2\text{OH}$.

The Reaction of Chromyl Fluoride and Trifluoroethylene

To 8.977 mmoles of CrO_2F_2 (1.0954 g) contained in a 200 ml fused silica vessel was added 56.04 mmoles of Freon-113, and 5.899 mmoles of trifluoroethylene (0.4837 g) at -196° . The vessel was then placed in a -78° bath and reaction was evident almost immediately, with the formation of a brown solid. The reaction was kept at -78° for thirty minutes and then transferred to a 0° bath for overnight. Upon evacuation of the

vessel at -196° there was a non-condensable gas (at -196°) evolved, identified as carbon monoxide by its infrared spectrum and molecular weight (Requires: 28 Found: 26). The weight loss indicated that the CO amounted to 1.19 mmoles (0.0332 g). The vessel was warmed to -78° and the volatile materials investigated by infrared analysis. Absorbances due to CO_2 , COF_2 , and a trace of F-113 were observed with no evidence for the presence of trifluoroethylene. Upon evacuation at room temperature there was no CrO_2F_2 among the volatile materials. The product weight of the brown non-volatile solid was 1.0497 g, less than the weight of the CrO_2F_2 added.

The reaction was repeated using 16.78 mmoles of CrO_2F_2 and 37 mmoles of trifluoroethylene without a solvent. The reaction mixture was warmed from -196° to -78° and kept at that temperature for approximately 24 hours. The vessel was then placed in a -45° bath (chlorobenzene slush with dry ice) for approximately eight hours, after which the reaction was allowed to warm slowly to room temperature over the course of 12 hours. After the reaction vessel had warmed to room temperature, it was shaken and no vapors of CrO_2F_2 were visible. However, while being shaken the reaction mixture detonated sharply, completely destroying the vessel. It is advised that future investigators use extreme caution in the further study of these reactions, particularly when no solvents are used.

The Reaction of Chromyl Fluoride and Tetrachloroethylene

To 25.50 mmoles of tetrachloroethylene was added 67.56 mmoles of Freon-113 and 11.01 mmoles of chromyl fluoride (1.3427 g) at -196° . The reaction mixture was placed in a 0° bath where reaction was evident

immediately upon melting of the olefin, forming a dark brown solid. Red-brown vapors were to be seen in the reaction vessel up to approximately 20 hours after the addition of the reactants but there had been no glass attack at the graded seal of the vessel over this period. Upon evacuation of the vessel at -196° , no volatile materials were noted but at -78° white and reddish-brown bands were observed in the -196° trap. These bands were found to be partially due to F-113, COCl_2 , and possibly COClF as identified by their infrared absorbances. Evacuation at room temperature yielded more F-113 and the deep reddish-brown compound along with tetrachloroethylene, leaving a light brown solid with a weight of 1.2898 g. The solution of F-113, tetrachloroethylene, and the reddish-brown compound was thoroughly degassed and then a sample was extracted with water. To the aqueous extract was added AgNO_3 solution which resulted in a white precipitate that dissolved in ammonium hydroxide.

Analysis for $\text{CCl}_2:\text{CCl}_2\cdot 2\text{CrO}_2\text{F}_2$: Cr; Requires: 25.4% Found: 40.3%, F; Requires: 18.5% Found: 9.78%, C; Requires: 5.85% Found: 1.73%, Cl; Requires: 34.6% Found: 25.4%.

Discussion

$\text{NO}_2\text{CrO}_2\text{F}_3$ and NOCrO_2F_3

Since chromyl fluoride has been shown to act as a Lewis acid in its reaction with Group Ia and Group IIa fluorides to form tetrafluorochromate(VI) salts (51), it seemed reasonable that formation of nitryl and nitrosonium salts from the strong Lewis bases NO_2F and NOF was likely. At 45° in a fused silica vessel the reaction of NO_2F and CrO_2F_2 leads to formation of a very hygroscopic, pale yellow solid which dissolves with vigor in water to give the familiar orange-yellow dichromate solution.

Reaction of nitrosyl fluoride and chromyl fluoride occurs at room temperature to produce a greenish-yellow powder that behaves like its nitronium analogue with water. The fact that NO_2 was found among the volatile products of the reaction of CrO_2F_2 and NOF indicates that there very probably was a side reaction occurring where the nitrosyl fluoride was oxidized by chromyl fluoride. A similar situation was noted in the reaction of NO with CrO_2F_2 (51). Both salts decompose at elevated temperatures ($\text{NO}_2\text{CrO}_2\text{F}_3$ at 130 , NOCrO_2F_3 at 100) to give off NO_2 . Lack of an x-ray powder pattern indicates both compounds are amorphous.

Dioxotrifluorometalate ions are known and have been well characterized as being isostructural for vanadium, tungsten, and molybdenum. The $\text{VO}_2\text{F}_3^{-2}$ ion has been studied in the form of its potassium, rubidium, and cesium salts and shown by x-ray studies to be a fluorine-bridged polymer, containing a cis-dioxo configuration coplanar with the bridging fluorines (66, 67). Vibrational spectral work on these compounds is in agreement with this structure. Publications on WO_2F_3^- and MoO_2F_3^- containing compounds report a similar structure, again using x-ray analysis and vibrational spectral data (68, 69). The structure of the $\text{MO}_2\text{F}_3^{-n}$ ion is shown in Figure 5:

Figure 5 - Structure of the MO_2F_3^- ion ($\text{M} = \text{V}, \text{W}, \text{Mo}$)

Metal ions containing a cis-dioxo configuration are well known (70) and have been shown to be present in compounds containing the $\text{MO}_2\text{F}_4^{-n}$ ion,

such as $\text{Cs}_2\text{CrO}_2\text{F}_4$ (51), $\text{Cs}_2\text{MoO}_2\text{F}_4$ (68), $\text{Cs}_2\text{WO}_2\text{F}_4$ (68) and $\text{K}_3\text{VO}_2\text{F}_4$ (67).

The infrared vibrational frequencies for $\text{NO}_2\text{CrO}_2\text{F}_3$ and NOCrO_2F_3 are presented in Table IX. Comparison of the band positions of $\text{NO}_2\text{CrO}_2\text{F}_3$ with those of $\text{K}_2\text{VO}_2\text{F}_3$, also in Table IX, shows good agreement between the two spectra. Griffiths (70) has presented evidence that all known transition metal d^0 dioxo species tend to have cis oxygens. The microsymmetry is C_{2v} and thus the O-M-O group should display an infrared active symmetric and antisymmetric metal oxygen stretch. In addition, the fluorine bridging in the polymer makes the fluorine atoms nonequivalent so that there is a symmetric and antisymmetric stretch for each pair of similar Cr-F bonds. These modes are readily assigned in $\text{NO}_2\text{CrO}_2\text{F}_3$. The absorbances at 1010 and 970 cm^{-1} represent the symmetric and antisymmetric chromium-oxygen stretch, respectively. The 720 and 610 cm^{-1} peaks are reasonably assigned to antisymmetric Cr-F stretch while the 635 cm^{-1} band is given to one symmetric Cr-F stretching mode. It is not possible to assign the other Cr-F symmetric stretch definitely because it appears to fall in about the same region as that of the bending mode of the NO_2^+ ion. This will be discussed in the next paragraph. The shoulder at 490 cm^{-1} remains unassigned; it is possibly an overtone. The absorbances below 350 cm^{-1} are in the region usually ascribed to metal-oxygen and metal-fluoride deformations, but definite assignment of these is tenuous and will not be attempted. The spectrum of NOCrO_2F_3 is much less well defined so only the gross features can be interpreted. The band at 1900 cm^{-1} is unambiguously a terminal chromium-oxygen double bond stretch but the fact that it is not split into a doublet seems to raise doubt about the compound having the same structure

Table IX - Infrared Vibrational Frequencies of $\text{NO}_2\text{CrO}_2\text{F}_3$ and NOCrO_2F_3 ,
in cm^{-1}

<u>$\text{NO}_2\text{CrO}_2\text{F}_3$</u>	<u>NOCrO_2F_3</u>	<u>Probable Assignment</u>	<u>$\text{K}_2\text{VO}_2\text{F}_3$ (67)</u>
3780w		$\nu_1 + \nu_3$ (NO_2^+)	
2380m		ν_3 (NO_2^+)	
	2290m	ν (NO^+)	
	1505m		
1380m	1380m	ν_1 (NO_2^+)	
1295m	1295m	(720 + 580 = 1300)	
1010s	1000s,b	ν_s ($\text{O}=\text{Cr}=\text{O}$)	922
970s		ν_a ($\text{O}=\text{Cr}=\text{O}$)	898
880w			
720m	730m	ν_a Cr-F	570
635s		ν_s Cr-F	550
610s		ν_a Cr-F †	529
580s		ν_s Cr-F †	431
550s	550s,b	ν_2 (NO_2^+)	
590w,sh			
350w		ν Cr-F-Cr	345
310w		δ F-Cr=O	305
260w	240w	δ F-Cr-F	223
		O=Cr=O	

as shown in Figure 5. However, it could simply be that the doublet is not resolved. The bands at 730 and 550 cm^{-1} are reasonably assigned to Cr-F stretching modes but again there is not the good agreement with previously published spectra that was found in $\text{NO}_2\text{CrO}_2\text{F}_3$.

Salts containing the nitryl and nitrosonium ions are well known and characterized. The linear NO_2^+ species displays two infrared active bands; the bending mode, ν_2 , and the antisymmetric stretch, ν_3 produce these absorbances. The symmetric stretch, ν_1 , is Raman Active. In a typical NO_2^+ salt such as nitryl perchlorate (71), the ν_1 mode was observed at 1396 cm^{-1} while the ν_2 fundamental is found at 570 cm^{-1} and ν_3 at 2360 cm^{-1} . For $\text{NO}_2\text{CrO}_2\text{F}_3$, the ν_3 mode is located at 2380 cm^{-1} in the infrared. The ν_2 band falls in the region of chromium-fluorine stretch but is probably represented by either the peak at 580 or 550 cm^{-1} with the other absorbance being a symmetric Cr-F stretch. The O-N-O bending vibration was observed at 538 cm^{-1} in solid N_2O_3 ($\text{NO}_2^+\text{NO}_3^-$) (72). As was mentioned earlier, the ν_1 symmetric stretch is Raman active only; however, often it can be estimated by the infrared allowed combination band $\nu_1 + \nu_3$ which commonly occurs in nitryl salts. In NO_2PtF_6 (73), this combination band occurred at 2362 cm^{-1} which was in good agreement for the sum of ν_1 and ν_3 values. If the peak at 3780 cm^{-1} for $\text{NO}_2\text{CrO}_2\text{F}_3$ is taken to be the $\nu_1 + \nu_3$ mode, then the difference between 3780 and 2380, the value for ν_3 , gives 1400 cm^{-1} which is surprisingly coincident with a prominent absorbance in the spectrum. The Raman-active ν_2 mode has been observed at 1400 cm^{-1} in solid N_2O_5 (72) and at 1396 cm^{-1} in NO_2ClO_4 (71). A possible explanation for the Raman active mode becoming

infrared active could be that the normally linear NO_2^+ ion is bent through some sort of lattice effect. A bent nitryl ion would then be of C_{2v} symmetry instead of $D_{\infty h}$ and would display three absorbances, all infrared active. These infrared bands would be coincident with three peaks in the Raman effect but unfortunately, attempts to obtain a Raman spectrum for $\text{NO}_2\text{CrO}_2\text{F}_3$ failed.

The absorbance at 2290 cm^{-1} for NOCrO_2F_3 is the NO^+ stretching mode. It has been observed at 2340 cm^{-1} in NOAsF_6 , 2331 cm^{-1} in NOMoF_6 , and 2377 cm^{-1} for NOSO_3F (108).

In summary, there is good evidence that $\text{NO}_2\text{CrO}_2\text{F}_3$ contains a fluorine-bridged, cis-dioxo trifluorochromate(VI) ion, similar to the corresponding vanadium, molybdenum, and tungsten anions. It appears that the NO_2^+ ion $\text{NO}_2\text{CrO}_2\text{F}_3$ may be bent as interpreted from infrared spectral evidence but this is not conclusive due to the lack of Raman data. The IR spectrum of NOCrO_2F_3 is ill-defined and little information can be obtained from it except to say that the NO^+ ion is present.

$\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$

Makhija and Stairs (53) found that certain solvents such as acetonitrile, dioxane, pyridine, and tetrahydrofuran will react with the Etard complex formed between chromyl chloride and toluene. The composition of the products was found to be $\text{C}_6\text{H}_5\text{CH}_3 \cdot 2\text{CrO}_2\text{Cl}_2 \cdot 2\text{D}$, where D represents the organic solvent apparently acting as a Lewis base. It was assumed that the donor solvent molecules were coordinated directly to the tetravalent chromium centers which resulted in the depolymerization of the Etard complex.

The previously known inorganic Etard complex $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$ (51) was found to also react with acetonitrile to give an adduct with composition

$\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$. No compound other than CH_3CN was found among the volatile materials of the reaction. The non-volatile product, a light green solid, is hygroscopic, but less so than the original complex, $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$. A hydrolyzed solution of the adduct does not give a precipitate when BaCl_2 solution is added, but will yield an insoluble solid with Ba^{++} after treatment with H_2O_2 . This provides evidence for the sulfur probably being present in the tetravalent state in the complex. Upon hydrolysis, the sulfur in the complex may well dissolve as the sulfite ion which can be oxidized to sulfate by H_2O_2 and thus precipitated as BaSO_4 .

The infrared spectrum of $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$ is tabulated in Table X. Prior spectroscopic work done on compounds containing coordinated acetonitrile are abundant in the literature. Nyholm and Kepert (74) reported infrared frequencies of acetonitrile coordinated to tantalum and niobium pentachlorides and pentabromides and found a very important band to be the symmetric C-N stretch (ν_2) since upon coordination this absorbance has been shown to be increased to higher wavenumbers. In Nyholm and Kepert's study, the change in ν_2 upon coordination ranged from 29 to 36 cm^{-1} which is similar to the 38 cm^{-1} found in $\Delta\nu_2$ for $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$. Other vibrations of acetonitrile can be assigned from the spectrum and are listed in the table. Since most of these bands for acetonitrile occur in a region of the spectrum that is free of inorganic absorbances, the assignments can be made with confidence. It was proposed in another study (75) that since a certain Ta(III) compound, $[\text{TaCl}_3(\text{CH}_3\text{CN})_2]_2$, displayed a relatively complex IR spectrum in the region

Table X - Infrared Vibrational Frequencies of $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$ and Related Molecules, in cm^{-1}

<u>$\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$</u>	<u>Probable Assignment</u>	<u>$\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$ (51)</u>	<u>CH_3CN (114)</u>
2995 vw	ν_5 (deg. C-H stretch)		2995 m
2930 w	ν_1 (sym. C-H stretch)		2940 m
2318 m	$\nu_3 + \nu_4$		2285 m
2292 m	ν_2 (sym. CN stretch)		2254 s
1660 m			1630 w
1560 m			
1450 w	ν_6 (deg. CH_3 def.)		1440 m
1410 w			
1365 w	ν_3 (sym. CH_3 def.)		1375 m
1287 m		1360 m 1310 m	
1130 w, sh	ν_5 0 = S = 0	1130 s	1090 m
1040 s, b	ν_a 0 = S = 0 or ν_7 (deg. CH_3 rock)	1050 s	1035 s

CONTINUED ON NEXT PAGE

TABLE X - CONTINUED

<u>SO₂·2CrO₂F₂·2CH₃CN</u>	<u>Probable Assignment</u>	<u>SO₂·2CrO₂F₂ (51)</u>	<u>CH₃CN (114)</u>
955 w, sh	ν Cr = O or ν ₄ (sym. C - C stretch)	974 s	915 s
890 w		838 m	
765 w		765 w	745 m
632 w, sh			
550 s, b	ν Cr - F	550 s, b	
415 w			
360 w	ν Cr - F - Cr	330 w, b	

3000 to 2000 cm^{-1} , it revealed the acetonitrile ligands to be in significantly different environments. If in fact the absorbances of the acetonitrile ligands are as sensitive as was proposed, it can be taken that the CH_3CN groups in $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2 \cdot 2\text{CH}_3\text{CN}$ are identical due to the simplicity of the infrared spectrum. The fact that the acetonitrile absorbances are exactly where one would predict for coordinated CH_3CN , coupled with the very good chemical analysis, tends to exclude the possibility of oxidation of acetonitrile by the pentavalent chromium found in $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$. Unfortunately, very little else can be said about the structure of the complex.

n-Hexane - Chromyl Fluoride Etard Reaction

It was originally anticipated that chromyl fluoride would prove to be a more active oxidant than chromyl chloride toward relatively non-reactive hydrocarbons such as hexane. Hobbs and Houston (54) found the yield of the Etard Complex formed between chromyl chloride and n-hexane to be only 31.5%. Subsequent hydrolysis yielded 2-hexanone, 3-hexanone, and what was reported as higher boiling unsaturated ketones. Chromyl fluoride has been found in this research to react quantitatively with n-hexane at room temperature but due to the fact that CrO_2F_2 will attack glass, a major problem was finding a vessel capable of containing this potentially vigorous reaction during the synthesis of an adequate quantity of product. After testing a number of different apparatus assemblies, the set-up shown in Figure 2 was deemed the best available. The chromyl fluoride was contained in the addition vessel, to which the Freon-113 solvent was added. Reaction was immediate upon mixing the CrO_2F_2 with the n-hexane in Freon-113 solution, but during the course

of the addition, there was appreciable glass attack. In Hobbs and Houston's work, no identifiable organic hydrolysate was found when 38 grams of chromyl chloride-2,2-dimethylbutane Etard complex was hydrolyzed. To get 8 grams of 2-hexanone and 3-hexanone, they hydrolyzed 150 g of hexane-chromyl chloride Etard complex. As is evident from these last statements, the chromyl chloride-alkane Etard reaction does not give high yields. It was found that the same can be said for the chromyl fluoride Etard reaction with hexane.

The infrared absorbances of the n-hexane Etard complex with chromyl fluoride are listed in Table XI. The spectrum is of moderate quality despite repeated attempts to resolve some of the broad, featureless peaks to a greater extent; however, a few significant features are identifiable. The strong absorbance at 1640 cm^{-1} is in the same region where peaks assigned to coordinated carbonyl groups have been reported. Duffin and Tucker (76) have proposed that the toluene-chromyl chloride Etard complex consists of benzaldehyde coordinated to reduced CrO_2Cl_2 , implying that oxidation of the organic substrate by chromium is essentially complete upon formation of the Etard complex and the toluene oxidation product, benzaldehyde, stabilizes the intermediate oxidation state of the chromium via coordination through the carbonyl group. In their study, Duffin and Tucker compared infrared spectra of Etard complexes of CrO_2Cl_2 and toluene, benzyl alcohol, and benzyl chloride with liquid benzaldehyde and a Cr(III) complex isolated by refluxing CrCl_3 in benzaldehyde of the composition, $\text{CrCl}_3(\text{C}_6\text{H}_5\text{CHO})_3$. The Etard complexes and the Cr(III) adduct all displayed similar bands in the region 1640 to 1615 cm^{-1} which were assigned to the stretching

Table XI - Vibrational frequencies of the n-Hexane Etard Complex

<u>$C_6H_{14} + CrO_2F_2$</u>	<u>Probable Assignment</u>
3200-3000 s, b	ν O-H
2950 m, sh	ν C-H
1640 s, b	ν C=O--M
1440 w	
1360 w	
1200 w	ν C-H def
1150 w	ν C-H def
1010 w	
980 m	ν Cr=O
950 m	ν Cr=O
945 w, sh	
885 w	ν Cr-O-Cr
740 w, sh	ν Cr-F
530 s, b	ν Cr-F

mode of the coordinated carbonyl group in benzaldehyde. The free carbonyl in benzaldehyde absorbs at 1701 cm^{-1} . This proposal describing the structure of the Etard complex has been used to define the product obtained in the oxidation of phenols to quinones by chromyl chloride (77). In the chromyl fluoride oxidation of n-hexane, the hexanone isomers obtained among the products have carbonyl absorptions at 1717 cm^{-1} for 2-hexanone (109) and 1710 cm^{-1} for 3-hexanone (110). Assuming the 1640 cm^{-1} band in the n-hexane Etard complex to be due to a coordinated carbonyl group, this would represent a shift of 70 to 77 cm^{-1} which seems reasonable in light of Huffin and Tucker's data. The peaks at 980 and 960 cm^{-1} are in the region of terminal, metal oxygen double bond stretch while the weak absorbance at 885 cm^{-1} is assigned to a Cr-O-Cr bridge stretch (93). (See Chapter IV for an explanation of terminal versus bridging metal-oxygen bond stretching frequencies.) If the complex is a polymer as has been suggested (46), one would expect the presence of a metal-oxygen bridges. The peaks at 740 and 530 cm^{-1} fall into the region of metal-fluoride stretch (94). The strong, broad absorbance from 3200 to 3200 cm^{-1} is assigned to O-H stretch. This could represent a protonated oxygen bound singly to chromium or a hydroxyl group bridging between two chromium centers in the polymer. The results of the chemical analysis of the compound suggest that this complex, like that obtained in the analogous reaction with CrO_2Cl_2 , is a non-stoichiometric product and therefore an attempt at a detailed analysis of the spectrum is not possible.

Controlled hydrolysis of the n-hexane-chromyl fluoride Etard complex was accomplished in a saturated sodium sulfite solution at

less than 3°. Ether extraction and subsequent concentration yielded a relatively small quantity of organic material (4 g) which tended to darken rapidly upon heating to give a brown precipitate coating the inside of the vessel. Gas chromatographic analysis of this concentrated sample revealed the presence of ethyl ether, which made up 17% of the solution, and at least ten other different compounds. By comparison of retention times of authentic samples to that of components of the hydrolysate, hexanoic acid and 2-hexanone and/or 3-hexanone could be identified as being products of the reaction. No distinction could be made between the two hexanone isomers under the conditions that were employed. The darkening of the solution with formation of a precipitate was probably due to air-oxidation and polymerization of the hydrolysis products.

The tabulated infrared spectrum of the hydrolysate is presented in Table XII. The broad peak from 3450 to 3250 cm^{-1} is assigned to the oxygen-hydrogen stretch of a carboxylate group with the carbonyl of this group absorbing at 1702 cm^{-1} . The carbon-hydrogen stretching frequencies are found at 2982 , 2960 , and 2940 cm^{-1} . Since the hydrolysate is a complex mixture, the "fingerprint" region is obscured, but the overall spectrum is very similar to that of hexanoic acid.

In summary, it has been found that chromyl fluoride reacts with n-hexane below 3° to form an Etard complex of apparently non-stoichiometric composition similar to that produced from CrO_2Cl_2 and n-hexane. The solid displays an infrared spectrum which suggests that oxidation of the organic substrate is essentially complete due to the presence of what is assigned as the absorbance of a coordinated carbonyl group.

Table XII - Infrared Absorbances of n-Hexane Etard Reaction Hydrolysate
in cm^{-1}

<u>Absorbance</u>	<u>Probable Assignment</u>
3450-3250 s,b	O-H stretch
2982, 2960, 2940 s	C-H stretch
1702 s	C=O stretch
1450 m	
1405 m	
1375 m	
1270 w	
1082 s	
1045 s	
878 s	

Controlled hydrolysis of the complex leads to formation of at least ten different organic products in low yields.

Reaction of Chromyl Fluoride with Haloolefins

Chromyl chloride has often been used as an oxidizing agent for alkenes (54) but it was reported that tetrachloroethylene and trichloroethylene do not react with CrO_2Cl_2 (111). As was mentioned in the introduction, Knunyants (59) has found that chromyl chloride does react with a number of fluoroolefins and chlorofluoroolefins. In addition, chromyl fluoride formed in situ from HF and CrO_3 at -78° reacted with 1,1-difluoroethylene and trifluoroethylene (60). In this research, it was found that trifluoroethylene, tetrachloroethylene, and 1,1-difluoroethylene react with chromyl fluoride at or below room temperature to give Etard products.

Chromyl fluoride and 1,1-difluoroethylene react to form a brown product of apparent composition, $\text{CF}_2\text{:CH}_2\cdot 2\text{CrO}_2\text{F}_2$. There is a small amount of destructive oxidation of the organic substrate leading to formation of CO and COF_2 . This fragmentation occurs to a much greater extent in the reaction of $\text{CF}_2\text{:CHF}$ and CrO_2F_2 with 10.0% of the total carbon weight lost as carbon monoxide. Destruction of the olefin was such that after reaction and removal of volatile materials, the weight of the brown product was less than that of the amount of chromyl fluoride added. Carbonyl fluoride and carbon dioxide were found to be the other products of the fragmentation of trifluoroethylene but the exact amount of these by-products could not be quantified because the presence of the volatile solvent, Freon-113, did not allow a meaningful weight to

taken after removal of the -78° volatile materials.

An attempt was made to minimize the destructive oxidation of trifluoroethylene by chromyl fluoride by running the reaction at low temperature over the course of a few days. Unfortunately, no suitable solvent was available which would be a liquid at that temperature. The reactants were added into a fused silica vessel at -196° with the olefin present in a greater than twofold molar excess. The vessel was kept at -78° for about one full day and was then warmed slowly to room temperature during the following day. There definitely had been a reaction as evidenced by the formation of a dark brown solid almost immediately where the chromyl fluoride had been condensed in the reaction vessel. When the vessel had warmed to room temperature on the third day, there were no vapors of chromyl fluoride visible which was interpreted as an indication of the reaction's completion. However, upon shaking the vessel (as had been done on the previous two days) the product detonated, completely destroying the fused silica container. Explosions have been reported with the chromyl chloride Etard reactions (54), particularly in concentrated solutions or solventless systems. It is advised that future investigators use caution in the further study of these reactions and avoid whenever possible, a chromyl fluoride reaction run without a solvent.

Tetrachloroethylene reacts with chromyl fluoride rapidly but what at first appeared to be incompletely. After 20 hours reaction time, red vapors still appeared in the vessel, even though the olefin was present in excess. Particularly puzzling was the fact that over

this extended period of time there was no glass attack upon the graded seal of the fused silica vessel which is very unusual for CrO_2F_2 reactions run for this length of time. Upon removal of the volatile materials, including COCl_2 but no CO , a light brown solid remained. A deep red solute which did not attack glass was found in the Freon-113 solution removed from the product. A thoroughly degassed sample of this solution was extracted with water and tested for chloride ion with silver nitrate solution. The positive test for chloride together with the non-glass attacking properties and color of the solute, led to the assumption that this was chromyl chloride. Isolation of the pure compound from the solution was not possible due to the very similar volatilities of tetrachloroethylene and chromyl chloride. It is well known that chromyl chloride and chromyl fluoride exchange halide atoms quite rapidly at room temperature (8, 112) but no examples of ligand exchange with compounds such as tetrachloroethylene appear to be found in the literature. A more likely candidate for the source of chloride could be phosgene (carbonyl chloride) produced by the destruction of the olefin. Acid chlorides such as $(\text{COCl})_2$ and CH_3COCl can be used to produce chromyl chloride from chromates or chromium trioxide (31, 32) so it seems reasonable that the chloride atoms in COCl_2 might have sufficiently ionic character to exchange with chromyl fluoride to produce CrO_2Cl_2 and COF_2 or COClF . As with the reaction involving trifluoroethylene, the weight of the product obtained from reaction of chromyl fluoride and tetrachloroethylene was less than the weight of CrO_2F_2 used due to the removal of the volatile carbon-containing compounds formed in the destruction of the olefin.

The magnetic susceptibility of $\text{CF}_2\text{:CH}_2 \cdot 2\text{CrO}_2\text{F}_2$, obtained by the Guoy method, was found to be 3.73 Bohr Magnetons. The spin-only value for two unpaired electrons is 2.83 B.M. while that for three unpaired electrons is 3.88 B.M. The presence of a small amount of reduced chromium from the oxidative destruction of the olefin would tend to give a larger value for the magnetic susceptibility so it seems unlikely that the complex possesses three unpaired electrons but rather that a representative value would lie somewhere between the values for two and three unpaired electrons. Leigh and Strickson (77) found intermediate values for the magnetic susceptibilities of the Etard complexes formed from chromyl chloride and various phenols but provided no explanation for these odd magnetic moments.

The tabulated values for the infrared vibrational frequencies of the products obtained in the reactions of chromyl fluoride with the three haloolefins are presented in Table XIII. Without information concerning the structure of the complex it is not possible to make many definite assignments. The striking feature of the three spectra is their similarity despite the fact that only the 1,1-difluoroethylene product is a stoichiometric complex with the other two containing an apparently large amount of reduced chromium. In looking for the inorganic features of the complexes, the familiar Cr=O stretch would appear to be found at 970, 990, and 985 cm^{-1} in the chromyl fluoride complex of 1,1-difluoroethylene, tetrachloroethylene, and trifluoroethylene, respectively. As with n-hexane Etard complex discussed earlier in this chapter, if one assumes these compounds to be polymers, it would be expected to

Table XIII - Vibration Frequencies of Chromyl Fluoride - Chlorofluoroolefin Reaction Products

<u>CF₂:CH₂*2CrO₂F₂</u>	<u>CCl₂:CCl₂ + CrO₂F₂</u>	<u>CF₂:CFH + CrO₂F₂</u>	<u>Approximate Assignment</u>
3300-2700 m,b		3300 - 2800 s, b	ν O - H
2910 - 2800 s, b			
1850 w			
1620 m	1600 s	1610 s	ν C = O--M
1560 w, sh			
1450 s		1470 w	
	1380 w		
1270 w		1290 w	
1230 w		1235 w, sh	
1198 m	1203 w	1200 m	
1165 m	1165 m	1185 m	
1100 w	1105 w	1100 m	
1025 w	1025 w, sh	1030 w	

CONTINUED ON NEXT PAGE

TABLE XIII - CONTINUED

<u>CF₂:CH₂*2CrO₂F₂</u>	<u>CCl₂:CCl₂ + CrO₂F₂</u>	<u>CF₂:CFH + CrO₂F₂</u>	<u>Approximate Assignment</u>
970 m	990 s	985 m	v Cr = O
895 w	900 w	900 w	
	860 w	865 w	
800 w	800 w	805 w	v Cr - O - Cr
712 m	712 s	700 m, sh	v Cr - F
550 s, b	540 s, b	550 s, b	v Cr - F
	300 w		

find bridging as well as terminal oxygens bound to chromium. The absorbances found at about 800 cm^{-1} in the three complexes are in the proper region for Cr-O-Cr stretch (93). Chromium fluoride stretches are assigned to the peaks occurring at about $710\text{--}712$ and $540\text{--}550\text{ cm}^{-1}$. The broad bands from 2700 to 3300 cm^{-1} found in the trifluoroethylene and 1,1-difluoroethylene complexes are assigned to O-H stretch. Again as in the n-hexane Etard complex, it seems possible that it could be either the result of a protonated, singly bound oxygen or a hydroxyl group bridging between chromium centers. Carbon-halogen stretching absorbances usually can occur from approximately 800 to 1350 cm^{-1} (113). This region of the three spectra is complex as one would expect, but definite assignments are not possible. The prominent peaks at 1620 cm^{-1} in the 1,1-difluoroethylene complex, 1600 cm^{-1} in tetrachloroethylene complex, and 1610 cm^{-1} in the trifluoroethylene complex are similar to those observed by Huffin and Tucker (76) in the infrared spectra of chromyl chloride Etard complex and also to that observed in the n-hexane-chromyl fluoride Etard complex reported earlier in this chapter. These bands have been assigned to the stretching vibration of a coordinated carbonyl group where the oxidized product formed upon hydrolysis was either an aldehyde or a ketone. This evidence is in apparent disagreement with the results of Knunyants (60) who reported trifluoroethanol as the hydrolysis product of chromyl fluoride and 1,1-difluoroethylene. Although a reducing agent (SO_2) was added to the hydrolysis mixture, tetravalent sulfur is not capable of reducing carbonyl groups to alcohols. Knunyants did not isolate the intermediate complex but simply hydrolyzed the reaction product directly after it was formed. In this research, enough 1,1-difluoro-

ethylene-chromyl fluoride complex was prepared to hydrolyze in NaHSO_3 solution. An ether extract of the hydrolysate showed only one product peak upon gas chromatographic analysis. This peak was found not to be due to trifluoroethanol upon comparison to an authentic sample of $\text{CF}_3\text{CH}_2\text{OH}$. The compound produced in the hydrolysis of $\text{CF}_2:\text{CH}_2 \cdot 2\text{CrO}_2\text{F}_2$ could not be identified, but it definitely was not trifluoroethanol.

In summary, it was found that 1,1-difluoroethylene, trifluoroethylene, and tetrachloroethylene all react with chromyl fluoride to give Etard products. Only 1,1-difluoroethylene gave a stoichiometric complex, having a composition of $\text{CF}_2:\text{CH}_2 \cdot 2\text{CrO}_2\text{F}_2$. The other two olefins underwent destructive oxidation to produce CO and carbonyl halides and tetrachloroethylene also yielded chromyl chloride as a result of some sort of halogen exchange, probably with COCl_2 . The magnetic susceptibility of $\text{CF}_2:\text{CH}_2 \cdot 2\text{CrO}_2\text{F}_2$ was found to be 3.79 B.M., a value which would have to be considered inconclusive toward assigning the oxidation state of chromium in the complex. Infrared spectral data suggests that both terminal and bridging oxygen-chromium bonds are found in the complexes as well as the fact that it appears that the oxidized organic substrates found in the complexes contain carbonyl groups coordinated to the chromium centers. Hydrolysis of $\text{CF}_2:\text{CH}_2 \cdot 2\text{CrO}_2\text{F}_2$ in this research did not yield trifluoroethanol as had been published earlier.

CHAPTER IV

Preparation and Characterization of Chromium(V) Oxide Trifluoride

Introduction

Although the most common higher oxidation state of chromium is Cr(VI), the pentavalent and tetravalent state has been shown to exist in a number of compounds. Chromium pentafluoride and chromium tetrafluoride were first prepared in 1941 (4). Tetrahedral alkali metal chromate (V) salts have been isolated from strongly basic solutions and characterized via x-ray studies (78), ESR spectra (79), and magnetic susceptibility measurements (80). From concentrated HCl solutions, octahedral salts of CrOCl_5^{2-} have been prepared and studied (81). Willis has produced a Cr(V) ion through the reaction of chromate ion and perfluoropinacol which was characterized by its electronic spectrum and magnetic susceptibility measurements (82).

Krauss (82, 83, 84) synthesized chromium(V) oxide trichloride using chromium trioxide and either thionyl chloride or sulfuryl chloride. The co-products of the reaction were found to be chlorine and sulfur dioxide or sulfur trioxide, depending on the starting material. The major product of the reaction is chromyl chloride but the less volatile CrOCl_3 can be isolated in two percent yield via sublimation of the reaction residue. The magnetic susceptibility of the compound at 23° was determined to be 1.81 Bohr Magnetons. Chromium(V) oxide trichloride is unstable at room temperature, disproportionating to CrO_2Cl_2 and presumably CrCl_3 . No vibrational spectra data or physical chemical information was given.

It is interesting that with chromium under extreme fluorinating conditions; *ie.* high temperature and high pressure of F_2 , chromium pentafluoride is the major product and not a hexavalent chromium species. This is due to the fact that CrF_6 apparently is unstable above approximately -80° , decomposing to CrF_5 and F_2 (35). Chromium pentafluoride can be produced by high temperature fluorination of Cr metal (4), CrF_3 (87), or CrO_3 (6). In the latter example, Edwards showed the reaction of fluorine and chromium trioxide to be a stepwise process. At a reaction temperature of 150° , CrO_2F_2 was found to be the predominant product while at 220° , chromium oxide tetrafluoride proved the major species. Above 250° , CrF_5 was obtained. It was assumed that fluorination of chromium trioxide proceeds by successive replacement of oxygen leading to formation of CrF_6 , which decomposes yielding chromium pentafluoride.

With certain other potent fluorinating agents a similar situation has been found to exist; that is, reaction of a hexavalent chromium compound yields a product reduced to the pentavalent oxidation state. The reaction of bromine trifluoride with chromium trioxide and potassium dichromate yields $CrOF_3 \cdot 0.25BrF_3$ (23, 24) and $KCrOF_4$ (25), respectively, while reactions of CrO_3 with ClF_3 and BrF_5 produce $CrOF_3 \cdot 0.30ClF_3$ and $CrOF_3 \cdot 0.25BrF_5$ (23, 24). The $CrOF_3$ adducts are all red solids while $KCrOF_4$ is reported as a purple powder. In all cases, the chromium has been reduced to the pentavalent oxidation state as identified by magnetic susceptibility measurements. No significant amounts of other chromium fluorides or oxide fluorides were found to be present among the products. Only very small quantities of CrO_2F_2 could be isolated.

Clark and Sadana (23, 24) found all attempts to remove residual amounts of the interhalogen fluorinating agent resulted in decomposition

of the CrOF_3 to lower valent chromium fluorides, probably Cr(III) . This is compared to the fact that $\text{KCrOF}_4 \cdot 0.5\text{BrF}_3$, the initial product isolated from the reaction of BrF_3 and $\text{K}_2\text{Cr}_2\text{O}_7$, was freed of BrF_3 to yield KCrOF_4 by heating the sample to 150° under vacuum.

Chromium (VI) is unique here in its reactivity since reaction with the interhalogen fluorides leads to reduction of the metal. Titanium dioxide reacts with BrF_3 to give TiF_4 while V_2O_5 appears to undergo a partial loss of oxygen in reaction with bromine trifluoride to give a mixture of vanadium pentafluoride and vanadium oxide fluorides (88). Vanadium pentoxide is reported to react with ClF_3 to form VOF_3 (89). As was mentioned in Chapter II, ClF_3 and ClF react with a number of Group VI oxides and oxide fluorides, in all cases yielding fluorinated products with the oxidation state of the metal center unchanged.

Experimental

Preparation of Chromium Oxide Trifluoride

To a passivated 100 ml Monel metal reaction vessel was added 14 mmoles of CrO_2F_2 and 35 mmoles of ClF via vacuum distillation. The reactants were then heated to 100° in a tube furnace for 12 hours after which time the vessel was evacuated at -196° , -78° , and room temperature. The -196° volatile product was oxygen as identified by its molecular weight (Requires: 32.0 found: 31.9). At -78° , the volatile materials consisted of ClF and ClO_2F , identified by their respective infrared spectra (42, 43) and Cl_2 , identified as a yellow-green liquid at -78° with a vapor pressure of approximately 100 mm at that temperature. No vacuum line transferrable material was noted at room temperature. Upon opening the vessel in the dry box, a brick-red, non-volatile powder was found coating the walls of the metal reactor. This solid darkens rapidly on exposure to the dry box

atmosphere. The sample was subjected to a Gouy measurement of magnetic susceptibility which yielded a value of 1.83 Bohr Magnetons, corresponding to one unpaired electron. The solid reacts violently with water to give a yellow-green solution and will ignite acetone upon contact. An aqueous solution of the hydrolyzed solid does not give a precipitate with AgNO_3 solution nor does pretreatment of the hydrolysate with NaNO_2 give a precipitate. Infrared and Raman spectral data are listed in Table XV. Analysis for CrOF_3 (Cr; requires: 41.6% found: 39.7%, 37.3%, F; requires: 45.6% found: 38.9%, 39.9%, Cl; Found: 3.82%, 5.52%).

To 16 mmoles of chlorine-containing CrOF_3 prepared by the above outlined procedure was added 20 mmoles of F_2 at -196° . The reaction mixture was heated to 120° for 4 hours. After removal of the excess fluorine at -196° , the -78° volatile products were investigated. The only compound evident in the infrared spectrum was identified as ClO_2F (43). There were no room temperature volatile products. The non-volatile product was found to be a bright purple solid which darkens much less quickly than the sample not treated with F_2 . Analysis (Cr; requires: 41.6% found: 41.6%, F; requires: 45.6% found: 43.1%, Cl; found: 0.72%). To verify the pentavalent nature of the compound, a sample was hydrolyzed, quantitatively diluted in a volumetric flask, and an aliquot titrated iodometrically with standardized thiosulfate solution. Apparent Cr(VI) Requires: 27.73% found: 27.64%. To another aliquot solution was added excess Na_2O_2 , then the solution was heated to 40° for 30 minutes and to boiling for 20 minutes. The solution was then titrated iodometrically. Requires: 41.50% found: 41.62%. In a glass capillary the compound did not attack glass appreciably below 200° but there was a sudden attack with apparent melting from 300 - 304° . The melt bubbles vigorously, turning

to a grey-green solid. An alternative preparative procedure of purple CrOF_3 was found to involve heating an excess ClF with CrO_2F_2 to 250° for 5 hours. The purple product obtained gives the same x-ray powder pattern as the material prepared using F_2 (see Table XVI). Infrared and Raman spectral data are listed in Table XIX.

Reaction of Chromium Trioxide and Chlorine Monofluoride at 250°

To 26 mmols of CrO_3 contained in a passivated 100 ml Monel metal reaction vessel was added 114 mmols of ClF at -196° . The vessel was allowed to warm to room temperature, then placed in an oven and heated to 285° for five hours. The reaction vessel was evacuated at -196° and a molecular weight determination performed on the volatile materials at that temperature. The gas was found to be oxygen. Requires: 32.0, found: 32.4. The vessel was then evacuated at -78° and an infrared spectrum taken of the products at that temperature revealed ClO_2F and ClO_2 to be present. There were no room temperature volatile materials. The vessel contained a lime-green powder which was not the least bit hygroscopic nor air sensitive. This solid was insoluble in water and displayed only Cr-F stretching modes in its infrared spectrum. The product weight corresponded to 26 mmols of CrF_3 . Analysis (Cr; requires: 47.7% found: 44.5%, F; requires: 52.3% found: 45.5%). The x-ray powder pattern for the product is listed in Table XVII.

Thermal Decomposition of Chromium Oxide Trifluoride

A freshly prepared sample of CrOF_3 (5.6 mmols), contained in a stainless steel reaction vessel was placed in a tube furnace and heated to 350° for four hours. The vessel was allowed to cool to room temperature and evacuated. A molecular weight of the gaseous contents revealed the presence of oxygen. Requires: 32.0 found: 31.9. The nonvolatile solid

product was a light-greenish tan powder which was not hygroscopic or otherwise air-sensitive. This powder was insoluble in water, CCl_4 , and DMSO. The infrared spectrum of the compound was similar to that of CrF_3 , with an absorbance due to Cr=O completely lacking. Analysis (Cr; requires: 47.7% found: 46.2%, F; requires: 52.3% found: 40.1%). The x-ray powder pattern is listed in Table XVII.

Reaction of Chromium Oxide Trifluoride and Antimony Pentafluoride

In a typical reaction, freshly prepared CrOF_3 (6.69 mmoles) was transferred directly from the preparation vessel to a 30 ml fused silica vessel. The SbF_5 (43.6 mmoles) was vacuum distilled from NaF at -76° . Upon melting of the SbF_5 and heating to 60° for 20 minutes with stirring, the mixture formed a deep, red-wine colored solution which turned more purple as time passed. Upon evacuation of the reaction vessel, only white bands (due to SbF_5) were found in the trap; however, as evacuation was continued, a yellow-orange band appeared and grew as time passed. The reaction mixture was evacuated to constant weight, leaving a fine, bright purple powder which had a corresponding weight pickup of 12.8 mmoles of SbF_5 or 95.5% of that expected for a 1:2 adduct. The product melts from 120 - 125° to a reddish brown mass which bubbles vigorously above 130° . The magnetic susceptibility of the adduct was found to be 2.27 Bohr Magnetons at 21° . The compound is very hygroscopic and reacts vigorously with water to give a yellow-green solution. Analysis: calculated for $\text{CrOF}_3 \cdot 2\text{SbF}_5$, requires; F: 44.2% found: 41.5%.

An absorption spectrum of the reaction mixture and of the yellow-orange volatile product was taken using the 30 ml fused silica reaction vessels as sample cells. The resultant data are listed in Table XX. Infrared data are presented in Table XXI.

Preparation of Chromium Pentafluoride from Chromium Oxide Trifluoride

To a freshly prepared sample of CrOF_3 (29 mmols) contained in a ClF-passivated stainless steel vessel was added 45 mmols of F_2 at -196° . The vessel was allowed to come to room temperature, then was heated to 180° for five hours. The excess fluorine was removed at -78° . Upon evacuation of the vessel at room temperature, a small, deep red band appeared in the -196° trap and grew only very slowly with time. The weight pickup corresponded to 27 mmols of CrF_5 . Opening the vessel in the dry box revealed a deep reddish coating throughout. An infrared spectrum of this red compound agreed with that of CrF_5 (61).

Discussion

Chromium oxide trifluoride was first noted in this research as a side reaction product of the interaction of ClF and CrO_3 at room temperature. Production of CrOF_3 reduced the yield of chromyl fluoride but it was found that running the reaction at 0° minimized the amount of the oxide trifluoride obtained as long as a large excess of chlorine monofluoride was avoided. The first samples of CrOF_3 obtained were brick-red solids which darkened rapidly in the dry box to a black solid and attacked glass readily. This product could be obtained from the reaction of either CrO_3 or CrO_2F_2 and ClF from 25° to 100° with the yield increasing with temperature. Chemical analysis of the compound showed the presence of from 3.32 to 5.52% chlorine, making the apparent composition $\text{CrOF}_3 \cdot 0.14 \text{ ClF}$ to $\text{CrOF}_3 \cdot 0.21 \text{ ClF}$. This is compared to the adducts of composition $\text{CrOF}_3 \cdot 0.25 \text{ BrF}_3$, $\text{CrOF}_3 \cdot 0.25 \text{ BrF}_5$, and $\text{CrOF}_3 \cdot 0.30 \text{ ClF}_3$ formed from the reaction of chromium trioxide and the respective inter-halogen fluorides (23,24,25). Similar to what was experienced with these other CrOF_3 adducts, an x-ray powder pattern could not be obtained from $\text{CrOF}_3 \cdot 0.21 \text{ ClF}$ because the capil-

laries exploded shortly after being loaded, presumably as a result of glass attack. Heating a sample in a melting point capillary resulted in almost immediate glass attack with the tube becoming completely opaque at 60-80°. A magnetic susceptibility measurement of the compound at 17° yielded a value of 1.82 Bohr Magnetons, consistent with a d^1 Cr(V) species (theoretical spin-only value: 1.77 B.M.). $\text{CrOF}_3 \cdot 0.21\text{ClF}$ reacts vigorously with water to give a yellow-green solution while acetone is ignited by the compound.

It is of interest to speculate on the nature of the contaminating chlorine species in $\text{CrOF}_3 \cdot 0.21\text{ClF}$. It is unlikely that the adduct is one that contains a discrete ClF species, especially in light of the recent work done on synthesis and characterization of inter-halogen ions. The interaction of ClF_3 with strong Lewis acids such as SbF_5 , AsF_5 , and BF_3 leads to formation of the ClF_2^+ ion (90) as counterion for SbF_6^- , AsF_6^- , and BF_4^- , respectively. Reaction of alkali metal fluorides with chlorine monofluoride leads to compounds containing the ClF_2^- ion which decompose above -78° (91). Chrste has shown that chloryl fluoride reacts with strong Lewis acids to form salts containing the ClO_2^+ ion (92). Pertinent vibrational spectral data for those compounds are listed in Table XIV.

The Raman and infrared spectral data for $\text{CrOF}_3 \cdot 0.21\text{ClF}$ are tabulated in Table XV. Bands at 1068 cm^{-1} in the infrared and 1065 cm^{-1} in the Raman effect fall in the region of ClO_2^+ symmetric stretch while the infrared absorbance at 1255 cm^{-1} can reasonably be assigned to an antisymmetric chloryl ion stretch. The ClO_2^+ antisymmetric stretching band should be Raman active but was not observed. The very weak Raman peaks at 1395 and 1325 cm^{-1} are about 150 to 200 wave numbers too high to be safely assigned to the chloryl antisymmetric stretch; these remain unassigned. The band

TABLE XIV

Vibrational Frequencies of Selected Chlorine Ions and ClF, in cm^{-1}

<u>$\text{ClF}_2^+\text{AsF}_6^-(90)$</u>		<u>$\text{ClF}_2^+\text{BF}_4^-(90)$</u>		<u>$\text{Pb}^+\text{ClF}_2^-(91)$</u>	
<u>Raman</u>	<u>IR</u>	<u>Raman</u>	<u>IR</u>	<u>Raman</u>	<u>IR</u>
821	818	808	813	661	
809		798		470	476
806	810	788	798		
384		394			
		373			
<u>$\text{ClO}_2^+\text{AsF}_6^-(92)$</u>		<u>$\text{ClO}_2^+\text{BF}_4^-(92)$</u>		<u>$\text{ClF}(91)$</u>	
<u>Raman</u>	<u>IR</u>	<u>IR</u>			
1296		1308			
1283	1296	1294			
1044	1044				
1038	1039	1100-990		747	
521					
519	521	518			

TABLE XV

Observed Vibrational Frequencies of $\text{CrOF}_3 \cdot 0.21 \text{ ClF}_3$, in cm^{-1}

<u>Raman</u>	<u>IR</u>	<u>Assignment</u>
1395 w		
1325 w		
	1255 w	$\nu_{\text{asym}} \text{ClO}_2^+$
1065 w	1078 wm	$\nu_{\text{sym}} \text{ClO}_2^+$
990 m	990 s	$\nu \quad \text{Cr=O}$
800 m	820 m	$\nu \quad \text{Cr-F}$
	770 s	$\nu \quad \text{Cr-F}$
710 m	710 s	$\nu \quad \text{Cr-F}$
590 m	600 s, b	$\nu \quad \text{Cr-F or } \delta \text{ClO}_2^+$
	370 w, sh	
	320 w	

corresponding to the ClO_2^+ bending mode is in the same region as the chromium-fluorine stretching region ($\sim 500\text{--}800\text{ cm}^{-1}$). The remaining bands can be assigned to Cr=O stretch: 990 cm^{-1} in the Raman and infrared; Cr-F stretch: $830\text{ to }600\text{ cm}^{-1}$; and deformations: $370\text{ and }320\text{ cm}^{-1}$. The assertion that chlorine is present in $\text{CrOF}_3 \cdot 0.21\text{ClF}$ as the ClO_2^+ ion is strengthened by the fact that the logical counterion, CrOF_4^- , is known (23) although no vibrational spectra are available. The $\text{ClO}_2^+\text{CrOF}_4^-$ could be produced from CrOF_3 reacting with ClO_2F formed in the reaction of ClF and CrO_3 or CrO_2F_2 .

It was found while attempting to prepare CrOF_4 , that treatment of chlorine-containing CrOF_3 with fluorine at 120° leads to a non-volatile purple product which has a lowered chlorine content. Analysis of the volatile materials from the reaction revealed ClO_2F to be the only species giving an infrared spectrum. Subsequent work revealed that purple CrOF_3 could also be prepared by the reaction of CrO_2F_2 and ClF at 250° . The compound does not attack glass or fused silica quickly and this fact allowed x-ray powder patterns to be taken. These showed the CrOF_3 prepared via the two different methods to be the same. (see Table XVI) Rapid heating of a sample of purple CrOF_3 in a melting point capillary results in little change below 200° but above that temperature glass attack becomes evident. At 300° there is a sudden, extensive attack with the appearance of melting. The melt bubbles vigorously, apparently giving off a gas. Further study showed that a sample of CrOF_3 heated to 350° in a metal vessel decomposes to give off O_2 . This is analogous to the behavior of CrO_2F_2 which decomposes to CrOF_2 and O_2 above 550° (47). The non-volatile decomposition product would logically be CrF_3 but the analysis for this compound was very poor and the x-ray powder pattern does not agree with that of CrF_3 . It is possible that thermal decomposition of CrOF_3 leads

TABLE XVI

X-Ray Powder Patterns of CrOF_3 Prepared by Two Methods

d(Å) Intensity

4.43 m

3.63 m

3.35 s

2.59 w

2.51 m

2.26 m

2.06 w

1.94 w

1.89 w

1.81 s

1.58 s

1.53 w

1.49 w

1.47 w

1.43 w

1.42 m

1.20 m

d(Å) Intensity

4.43 m

3.63 m

3.38 s

2.58 w

2.49 m

2.23 s

2.05 w

1.95 w

1.89 w

1.82 s

1.59 m

1.53 w

1.48 w

1.46 w

1.43 w

1.41 w

1.20 m

to a previously unknown, complex Cr(III) oxide fluoride. A mixture of chromium oxides and CrF_3 as a decomposition product of CrOF_3 is seemingly ruled out because of the lack of agreement in the x-ray powder patterns with known oxides and fluorides (see Table XVII).

Chromium oxide trifluoride does not dissolve in Freon-113 or perfluoroheptane. It does dissolve with decomposition in dry glacial acetic acid, 100% H_3PO_4 , and DMSO. All attempts to obtain a visible/UV spectrum failed.

When chromium trioxide was treated with chlorine monofluoride and heated to 285° , a non-hygroscopic lime-green solid was obtained which was found to be very similar to the compound produced by the thermal decomposition of CrOF_3 . As with the CrOF_3 thermal decomposition product, a poor analysis and unique x-ray powder pattern was obtained (see Table XVII).

Pentavalent chromium disproportionates to Cr(III) and Cr(VI) in water as described in Equation IV-1:

This fact provided an additional way of proving the pentavalent nature of the compound. A sample was hydrolyzed after weighing and quantitatively diluted in a volumetric flask. A comparison was made of aliquots treated with Na_2O_2 before iodometric titration with aliquots titrated directly from the hydrolyzed sample solution. In the peroxide-treated aliquots, Cr(III) was oxidized to Cr(VI) so these samples analyzed for 50% more chromium than the untreated solutions, as would be expected for a pentavalent chromium species.

In light of the veritable renaissance of inorganic chemistry brought about by vibrational spectroscopy in the past decade and a half, metal oxide trihalides have received limited attention. There has been much

TABLE XVII

X-Ray Powder Patterns of Products Obtained from Thermal
Decomposition of CrOF_3 and Reaction of CrO_3 and ClF at -285°

$\text{ClF} + \text{CrO}_3 \xrightarrow{285^\circ}$		$\text{CrOF}_3 \xrightarrow{350^\circ}$		CrF_3	
<u>d(Å)</u>	<u>Intensity</u>	<u>d(Å)</u>	<u>Intensity</u>	<u>d(Å)</u>	<u>Intensity</u>
6.08 w					
3.66 s				3.57	
				3.37	
3.07 w				3.21	
2.94 w		2.77 w			
2.62 m		2.71 s		2.62	
2.52 w		2.25 w			
2.18 m		2.12 s		2.18 m	
2.07 w					
1.96 w		1.96 w		1.93 m	
1.82 m		1.92 w		1.89	
1.72 w		1.89 w		1.85	
1.66 m				1.81	
1.59 w				1.78	
1.46 w		1.45 w		1.66	
1.44 w				1.64 m	
		1.37 m		1.59	
		1.31 w			

interest in correlating metal-oxygen stretching frequencies to bond orders, that is, identifying the double bond character of a terminal oxygen-metal bond compared to the single bond character of a bridging oxygen. There appears to be general agreement that strong Raman or infrared bands in the 1100 to 950 cm^{-1} region are indicative of terminal $\text{M}=\text{O}$ bonds while the 650 to 850 cm^{-1} region is characteristic of the $\text{M}-\text{O}-\text{M}$ antisymmetric stretch (93, 94). Table XVIII lists the reported metal-oxygen stretching frequencies for fifteen transition metal oxide trihalide solids, each placed in its respective group depending on the position of the $\text{M}-\text{O}$ stretching band.

An x-ray study of niobium oxide trichloride (101) revealed the structure of the compound to be di- μ -chloro bridged Nb_2Cl_2 units connected by niobium-oxygen bridges (see Figure 5) giving the niobium atoms a distorted octahedral coordination. MoOBr_3 , VOCl_3 , and WOBr_3 have x-ray powder patterns similar to NbOCl_3 and it has been proposed that they are isomorphous (102). X-ray studies on MoOCl_3 have shown there are two stable solid structures; one is a low temperature form isostructural with NbOCl_3 (103) and the other a higher temperature form containing terminal oxygens and di- μ -chlorobridges (104). The only infrared data which seems to be available for either form is the terminal oxygen stretching value of 1007 cm^{-1} for the high temperature form (93). The relative non-volatility of these compounds has been the suggested result of their extensive polymerization (105). Ozin and Reynolds (106) found the gas phase Raman spectrum of NbOCl_3 at 350° to be very similar to that of VOCl_3 at 130°, indicating a C_{3v} structure for gaseous NbOCl_3 , like VOCl_3 . Solid VOCl_3 contains terminal oxygens (95) and presumably chlorine bridges.

Figure 5 - Structures of Metal Oxide Trihalides

NbOCl_3 (101) MoOCl_3 (104) VOF_3 (50)

Bond Lengths

$$a = 1.57 \text{ \AA}$$

$$b = 1.70 \text{ \AA}$$

$$c = 1.93 \text{ \AA}$$

$$d = 1.95 \text{ \AA}$$

$$e = 2.34 \text{ \AA}$$

TABLE XVIII

Metal-Oxygen Stretching Frequencies (in cm^{-1})
 For Solid Transition Metal Oxide Trihalides

<u>Terminal Oxygen</u>			<u>Bridging Oxygen</u>		
		Ref.			Ref
VOF_3	1039	94	NbOCl_3	767	99
VOCl_3	1022	95	NbOBr_3	732	93
VOBr_3	1009	95	MoOBr_3	810	93
MoOF_3	1000	96	WOCl_3	796	98
MoOCl_3	1007	93	WOBr_3	722	98
ReOCl_3	1018	97	TcOBr_3	770	93
ReOBr_3	1018	93	TaOCl_3	837	100
TcOCl_3	1017	93			

Unfortunately, rather little attention has been paid to the halide stretching and bending bands of the solid molecules. Oddly, there are no assignments for any halide bridging which one would expect if the structure of these compounds was similar to that of VOF_3 or MoOCl_3 . An unassigned infrared spectrum of MoOF_3 has appeared in the Russian literature (96) and definitely appears to contain the terminal oxygen stretching mode. An oriented single-crystal Raman study of NbOCl_3 (94) has assigned a strong, sharp band at 770 cm^{-1} to an Nb-O-Nb antisymmetric stretch, a vibration also active in the infrared. Bridging chlorine stretches were assigned to bands at 293, 287, and 223 cm^{-1} while terminal chlorine stretches were found at 421 and 337 cm^{-1} .

The values for the infrared and Raman spectra of CrOF_3 are listed in Table XIX. The infrared spectrum is of very high quality and the intensities and positions are identical and reproducible using either a nujol mull or KBr disc. It has been reported that a KBr disc can present distorted bands in the infrared (107) but this does not appear to be the case here. The Raman spectrum is of rather poor quality, partially due to the fact that the samples seemed to fluoresce. In general, fluorides do not tend to be good Raman scatterers. Comparing the infrared and Raman spectrum results in the unambiguous assignment of the band at 1000 cm^{-1} to a terminal, chromium-oxygen double bond stretch. Definite assignments for the rest of the bands are not possible without having information on the structure of the compound; however, certain generalizations can be made based on accepted trends in the vibrational spectra of metal fluorides. The physical properties of the compound (non-volatility, insolubility in non-polar solvents) tends to suggest that CrOF_3 is extensively polymerized and this adds to the problem of assignment without a

TABLE XIX

Vibrational Frequencies of CrOF_3 , VOF_3 (94), and MoOF_3 (95), in cm^{-1}

<u>CrOF_3</u>			<u>VOF_3</u>	<u>MoOF_3</u>
<u>IR</u>	<u>Raman</u>	<u>Assignment</u>	<u>Raman</u>	<u>IR</u>
1000 s	1002 s	$\nu\text{Cr}=\text{O}$	1039 vs	1000 s
718 s	790 m	$\nu\text{Cr}-\text{F}$		
680 s	720 m	$\nu\text{Cr}-\text{F}$	741 s	
600 s	685 m	$\nu\text{Cr}-\text{F}$	678 w	680
565 s	600 m	$\nu\text{Cr}-\text{F}$	620 m	625
512 m	545 m	$\nu\text{Cr}-\text{F}-\text{Cr}$	530 m	545
478 m		$\nu\text{Cr}-\text{F}-\text{Cr}$		
	485 w	δ		490
378 w	440 w	δ	408 rw	
350 vw	380 w	δ		
330 w		δ	358 m	
	310 w	δ	326 s	
288 m		δ	312 vw	
			232 s	
			216 s	

structural determination. Although the structure of VOF_3 is known (50) and a Raman spectrum has been reported (94), no assignments were made. In comparing the spectra of VOF_3 and MoOF_3 with those presented for CrOF_3 in Table XIX, one sees there is a reasonably good similarity to be found between the spectra. Especially important is the metal-fluoride stretching region (800 to 550 cm^{-1}). The complexity of the spectra in this region lends evidence for the presence of different types of metal-fluoride bonds, eliminating the possibility of a simple monomeric C_{3v} species which would display only two IR and Raman active bands in this region. Edward's work on VOF_3 revealed the presence of four different bond lengths to the vanadium center (see Figure 5). These different metal-fluorine bond lengths would be expected to display a complex spectrum in the stretching region due to the resultant low symmetry and in fact, the Raman spectrum of VOF_3 is very similar to that of CrOF_3 except for the band at 790 cm^{-1} . The peaks found between 790 and 545 cm^{-1} in CrOF_3 can be reasonably assigned to Cr-F stretching modes, but more detailed assignments are not possible. The 790 cm^{-1} band in CrOF_3 would appear to be troublesome toward showing chromium and vanadium oxide trifluorides to be structurally similar. The peak is too intense to be an overtone ($485 + 310 = 795 \text{ cm}^{-1}$) but may be the result of a solely Raman active fluoride stretching mode. The fact that a coincident absorbance does not appear in the infrared excludes the possibility of this being the result of a Cr-O-Cr bridge stretch.

The infrared absorbances at 512 and 478 cm^{-1} fall in the region of fluoride-metal bridging. This mode is Raman inactive for linear M-F-M bridges and weak for bent bridging systems. The weak Raman band at 485 cm^{-1} may well be the result of a bent bridging vibration, coincident with the 478 cm^{-1} infrared peak. The bands below 400 cm^{-1} are generally accepted

as deformation modes. These would include O-Cr-F and F-Cr-F bending vibrations, but definite assignments are not possible.

Chromium oxide trifluoride was found to react with antimony pentafluoride to form a purple solution. An absorption spectrum of the SbF_5 solution in the quartz reaction vessel showed maxima at 550, 470, 320, and 270 nm. Upon removal of volatile materials at room temperature a yellow-orange solute became evident in the excess SbF_5 pumped off the non-volatile product. This solute displayed absorption bands at 465, 320, and 218 nm which corresponded well to those of the 1:2 adduct of CrO_2F_2 and SbF_5 (see Table XX). The remaining peak at 550 nm is in the region which is characteristic of Cr(V) species (82). Other pentavalent chromium examples are also listed in table XX.

The non-volatile product of the reaction is a purple solid with a composition of $\text{CrOF}_3 \cdot 2\text{SbF}_5$. It is formed in yields less than 100% due to formation of CrO_2F_2 , perhaps as a result of glass attack, with its subsequent removal as the slightly volatile $\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})$ (51). Formation of chromyl fluoride from CrOF_3 would logically also produce Cr(III) fluorides or oxide fluorides which account perhaps for the relatively poor chemical analysis. The adduct attacks glass slowly at room temperature and is rigorously hydrolyzed by water to form a yellow-green solution. $\text{CrOF}_3 \cdot 2\text{SbF}_5$ melts from 120-125° and decomposes above 130° to a brown solid with the evolution as a gas, probably oxygen. The magnetic susceptibility was measured as 2.27 Bohr Magnetons; a value which is rather high for a compound with one unpaired electron (theoretical spin-only value; 1.73 B.M.) but the presence of Cr(III) in the sample would account for the high value.

Data from an infrared spectrum of $\text{CrOF}_3 \cdot 2\text{SbF}_5$ are presented in Table XXI. The spectrum is of moderate quality due to attack on the salt plates;

TABLE XX

Electronic Spectrum of the Product
of CrOF_3 and SbF_5 and other Cr(V) compounds, in nm

<u>$\text{CrOF}_3 + \text{SbF}_5$</u>	<u>Yellow-Orange Volatile Compound from CrOF_3 and SbF_5 Solution</u>	<u>$\text{CrO}_2\text{FSb}_2\text{F}_{11}$</u>
550		
470	455	465 vs
322 vs	320	320 vs
270-190 vvs	218	250-190 vs, vbr

<u>$\text{KCrO}(\text{PFP})_2$ (82)</u>	<u>CrOCl_3 (84)</u>
574	520
310	390

however, certain assignments can be made. The peaks at 650 and 695 cm^{-1} are very similar to those found in the infrared spectrum of $\text{CrF}_5 \cdot 2\text{SbF}_5$ (61) which were assigned to Sb-F stretching modes of the $\text{Sb}_2\text{F}_{11}^-$ ion. The broad bands at 540 cm^{-1} is in the region reasonably assigned to fluorine bridging but it is not possible to tell whether it involves antimony, chromium, or both. In $\text{CrF}_4\text{Sb}_2\text{F}_{11}$ a broad peak at 525 cm^{-1} was assigned to Sb-F-Sb stretch. The symmetry to a CrOF_2^+ species would be of particular interest but only one other fluorine stretching mode is observed. The shoulder at 760 cm^{-1} is thus assigned to Cr-F stretch. The absorbance at 990 cm^{-1} originates from the Cr=O stretching mode. A Raman spectrum was not attempted.

$\text{CrOF}_2\text{Sb}_2\text{F}_{11}$ does not react with oxygen up to 80°. This is compared to $\text{CrF}_4\text{Sb}_2\text{F}_{11}$ which forms $\text{O}_2\text{CrF}_4\text{Sb}_2\text{F}_{11}$ at room temperature (61).

Reaction of CrOF_3 with fluorine at 180° yields CrF_5 . This provides a good preparation for this compound under relatively mild conditions.

TABLE XXI

Vibrational Frequencies of $\text{CrOF}_2\text{Sb}_2\text{F}_{11}$ and $\text{CrF}_4\text{Sb}_2\text{F}_{11}$ (61), in cm^{-1}

<u>$\text{CrOF}_2\text{Sb}_2\text{F}_{11}$</u>		<u>$\text{CrF}_4\text{Sb}_2\text{F}_{11}$</u>
<u>IR</u>	<u>Assignment</u>	<u>IR</u>
990 s	$\nu\text{Cr} = \text{O}$	
	$\nu\text{Cr} - \text{F}$	830 s
760 sh	$\nu\text{Cr} - \text{F}$	780 m
690 s	$\nu\text{Sb} - \text{F}$	695 s
650 s	$\nu\text{Sb} - \text{F}$	665 s
540 s, br	$\nu\text{Sb} - \text{F} - \text{Sb}$	525 s, br
280 w, sh	$\delta\text{Cr} - \text{F}$	280 w

BIBLIOGRAPHY

1. O. Unvänderben, Annalen Min. (2) 1, 135 (1827).
2. D.I. Mendelejeff, Principles of Chemistry, German Edition, St. Petersburg, (1892), p. 59.
3. K. Fredenhagen, Z. Anorg. Allgem. Chem., 247, 135 (1941).
4. H.V. Wartenberg, Z. Anorg. Allgem. Chem., 247, 135 (1941).
5. A. Engelbrecht, A.V. Grosse, J. Am. Chem. Soc., 74, 5262 (1952).
6. A. J. Edwards, W.E. Falconer, W.A. Sunder, J. Chem. Soc. A., 541 (1974).
7. H.L. Krauss, F. Schwarzbach, Chem. Ber., 94, 1205 (1961).
8. G.D. Flesh, H.T. Svec, J. Am. Chem. Soc., 80, 3189 (1958).
9. E.E. Aynsley, R. Nichols, P.L. Robinson, J. Chem. Soc., 623 (1953).
10. H.C. Clark, Chem. Rev. 58, 869 (1958).
11. H. Mainert, Z. Chem., 7, 41 (1967).
12. D.E. Young, L.R. Anderson, D.E. Gould, W.B. Fox, J. Am. Chem. Soc., 92, 2313 (1970).
13. C.J. Schark, R.D. Wilson, Inorg. Chem., 9, 311 (1970).
14. J.P. Faust, A.W. Jache, A.J. Klanica, U.S. Patent 3,545,924, D December 8, 1970.
15. J.F. Ellis, C.W. Forrest, J. Inorg. Nucl. Chem., 16, 150 (1960).
16. R.C. Shrewsberry, E.L. Williamson, J. Inorg. Nucl. Chem., 28, 2535 (1966).
17. M. Luce, O. Hartmanshenn, J. Inorg. Nucl. Chem., 29, 2826 (1967).
18. M.J. Heras, P.J. Aymonino, H.J. Schumacher, Z. Phys. Chem., 22, 161 (1959).
19. R. Benoit, G. Besnard, O. Hartmanshenn, M. Luce, J. Mongin, J. Pelissie, Commis. Energ. At., Rapp., (1970) CEA-R-3953 (Chem Abs., 27651c).

20. J.J. Pitts, A.W. Jache, Inorg. Chem., 7, 1661 (1968).
21. C. Lau, J. Passmore, J. Fluor. Chem., 6, 77 (1975).
22. C. Lau, J. Passmore, Inorg. Chem., 13, 2275 (1974).
23. H.C. Clark, Y.N. Sadana, Can. J. Chem., 42, 50 (1964).
24. H.C. Clark, Y.N. Sadana, Can. J. Chem., 42, 702 (1964).
25. A.S. Sharpe, A.A. Woolf, J. Chem. Soc., 798 (1951).
26. T.A. O'Donnell, D.F. Stewart, Inorg. Chem., 5, 1434 (1966).
27. F.S. Fawcett, A.L. McClelland, U.S. Patent 3,097,067, July 9, 1963.
28. A.L. McClelland, F.S. Fawcett, D.D. Coffman, unpublished work cited in "Preparative Inorganic Reactions", Interscience, W.C. Jolly, 1965, Vol. 2, p. 286.
29. F.S. Fawcett, C.W. Tullock, D.D. Coffman, J. Am. Chem. Soc., 84, 4275 (1962).
30. H. Eilingsfeld, M. Seefelder, H. Weidinger, Angew. Chem., 72, 836 (1960).
31. R. Adams, C.H. Ulich, J. Am. Chem. Soc., 92, 599 (1920).
32. H.S. Fry, J. Am. Chem. Soc., 33, 698 (1911).
33. A.A. Opalovsky, E.U. Lobkov, J. Fluor. Chem., 5, 181 (1975).
34. J.R. Case, F. Nyman, Nature, 193, 473, Feb. 3, 1962.
35. D.K. Padma, A.R. Vasudera Murthy, J. Fluor. Chem., 5, 181 (1975).
36. K.O. Christe, Inorg. Chem., 11, 1220 (1972).
37. E.T. McHale, G. von Elbe, J. Phys. Chem., 72, 1849 (1968).
38. W.R. Hasek, W.C. Smith, V.A. Engelhardt, J. Am. Chem. Soc., 82, 543 (1960).
39. G.H. Cady, G.B. Hargreaves, J. Chem. Soc., 1568 (1961).
40. A.J. Edwards, B.R. Steventon, J. Chem. Soc. A, 2503 (1968).

41. W.E. Hobbs, J. Chem. Phys., 28, 1220 (1958).
42. E.A. Jones, T.F. Parkinson, T.G. Burke, J. Chem. Phys., 18, 235 (1950).
43. D.F. Smith, G.M. Segun, W.H. Fletcher, Spec. Acta, 20, 1763 (1964).
44. A.H. Nielson, P.J.H. Woltz, J. Chem. Phys., 20, 1878 (1951).
45. O. Unverdorben, Ann. Physik. Chem., 7, 311 (1826).
46. W.H. Hartford, M. Darrin, Chem. Rev., 58, 1 (1958).
47. N.V. Rochat, J.N. Gerlach, G.L. Gard, Inorg. Chem., 9, 998 (1970).
48. C.D. Garner, R. Maher, Chem. Comm., 633 (1973).
49. S.D. Brown, G.L. Gard, T.M. Loehr, submitted to J. Chem. Phys., (1975).
50. A.J. Edwards, P. Taylor, Chem. Comm., 1474 (1970).
51. S.D. Brown, P.J. Green, G.L. Gard, J. Fluorine Chem., 5, 203 (1975).
52. S.D. Brown, G.L. Gard, Inorg. Chem., 12, 483 (1975).
53. R.C. Makhija, R.A. Stairs, Can. J. Chem., 46, 1255 (1968).
54. A.L. Etard, Bull Soc. Chim., 27, 249-51 (1877) and references in Chem. Rev., 58, 25 (1958).
55. C.C. Hobbs, B. Houston, J. Am. Chem. Soc., 76, 1254 (1954).
56. R.A. Stairs, D.G.M. Diaper, A.L. Gatzke, Can. J. Chem., 41, 1059, (1963).
57. I. Necsoui, A.T. Balaben, I. Pascaru, E. Sliam, M. Elian, C.D. Nenitzescu, Tetrahedron, 19, 1133 (1963).
58. D.H. Wheeler, Can. J. Chem., 38, 2137 (1960).
59. G.G. Belenku, L.S. German, I.L. Knunyants, Izv Akad Nauk SSSR, Ser Khim, 2, 379 (1970).
60. L.S. German, I.L. Knunyants, Dokl Akad Nauk SSSR, 166, 602 (1966).
61. S.D. Brown, Master's Thesis, Portland State University, 1975.
62. T.G. Burke, D.F. Smith, A.H. Nielsen, J. Chem. Phys., 20, 447, (1952).

63. J.H. Simons, ed., "Fluorine Chemistry", Vol. 2, Academic Press, New York, 1954, p. 498.
64. D.C. Berutt, R.H. Miller, I.C. Histasuna, Spectrochim Acta, 23A, 237 (1967).
65. P.J.H. Woltz, E.A. Jones, A.H. Nielsen, J. Chem. Phys., 20, 378, (1952).
66. R.R. Ryan, S.H. Mastin, M.J. Risefeld, Acta Cryst., 827, 1270 (1971).
67. G. Pansewang, K. Dehnicke, Z. Anorg. Allgem. Chem., 269, 265 (1969).
68. L.O. Atomyan, O.N. Krasochka, M.Ya. Rehlín, Chem. Comm., 610 (1961).
69. R. Mattes, G. Müller, H.J. Becher, Z. Anorg. Allgem. Chem., 389, 177 (1972).
70. W.P. Griffith, J. Chem. Soc. A., 211 (1969).
71. J.R. Soulen, W.F. Schwartz, J. Phys. Chem., 66, 2066 (1962).
72. R. Teranishi, J. Decius, J. Chem. Phys., 22, 877 (1953).
73. F.P. Gortsema, R.H. Toeniskoetter, Inorg. Chem., 5, 1217 (1966).
74. D.C. Kepert, R.S. Nyholm, J. Chem. Soc., 2872, (1955).
75. D.G. Blight, R.C. Deutscher, D.C. Kepert, J. Chem. Soc. Dalton, 88, (1972).
76. H.C. Dufin, R.B. Tucker, Chem. Ind., 1262 (1966).
77. M.J. Leigh, J.A. Stricken, J. Chem. Soc. Perkin II, 1476 (1973).
78. M. Greenblatt, E. Banks, B. Pest, Acta Cryst., 23, 166 (1967).
79. E. Banks, M. Greenblatt, B.R. McGarney, J. Chem. Phys., 47, 377, (1967).
80. R. Scholder, H. Schwartz, Z. Anorg. Allgem. Chem., 326, 1 (1963).
81. H.B. Gray, C.R. Hare, Inorg. Chem., 1, 363 (1962).
82. C.J. Willis, Chem. Comm., 944 (1972).
83. H.C. Krauss, G. Munster, Z. Naturforschg. 17b, 344 (1962).

84. H.C. Krauss, M. Leder, G. Munster, Chem. Ber., 96, 3008 (1963).
85. R.B. Johannesen, H.C. Krauss, Chem. Ber., 97, 2094 (1964).
86. O. Glemser, H. Roesky, K.H. Hellberg, Angew. Chem., Int. Ed., 2, 266, (1963).
87. J. Sviliuk, B. Zemva, Z. Anorg. Allgem. Chem., 385, 137 (1971).
88. H.J. Emeleus, A.A. Woolf, J. Chem. Soc., 164 (1950).
89. S. Blanchard, J. Chem. Phys., 61, 747 (1964).
90. R.J. Gillespie, M.J. Morton, Inorg. Chem., 9, 811 (1970).
91. K.O. Christe, W. Sawodny, J.P. Guertin, Inorg. Chem., 6, 1159, (1967).
92. K.O. Christe, C.J. Schack, D. Piliponch, Inorg. Chem., 8, 2489, (1969).
93. J.H. Canterford, R. Colton, I.B. Tomkins, Inorg. Nucl. Chem. Letters, 4, 471, (1968).
94. I.R. Beattie, K.M.S. Livingston, D.J. Reynolds, G.A. Ozin, J. Chem. Soc. A., 1210, (1970).
95. R.J.H. Clark, P.D. Mitchell, J. Chem. Soc. A., 2429 (1972).
96. G.E. Blokhina, I.N. Belyaer, A. Opalovski, L.I. Belan, Russ. J. Inorg. Chem., 17, 1113 (1972).
97. P.W. Fraiss, C.J.L. Lock, Chem. Comm., 75 (1971).
98. G.W.A. Fowles, J.L. Frost, Chem. Comm., 252 (1966).
99. D. Brown, J. Chem. Soc., 4944 (1964).
100. K. Dehnicke, Naturwiss., 52, 58 (1965).
101. D.E. Sands, A. Zalkin, R.E. Elson, Acta. Cryst., 12, 21 (1959).
102. P.C. Crouch, G.W.A. Fowles, J.L. Frost, P.R. Marshall, R.A. Walton, J. Chem. Soc. A., 1061, (1968).
103. M. Mercer, J. Chem. Soc. A., 2019 (1969).
104. M.G.B. Drew, I.B. Tomkins, J. Chem. Soc. A., 22 (1970).

105. J.H. Canterford, R. Cotton, "Halides of the Second and Third Row Transition Metals", Wiley-Interscience, New York, 1968, p. 51.
106. G.A. Ozin, A.J. Reynolds, Chem. Comm., 884 (1969).
107. I.R. Beattie, Chem. Soc. Rev., 4, 107 (1975).
108. D.W.A. Sharp, J. Thorley, J. Chem. Soc., 3557 (1963).
109. P.N. Gates, E.F. Mooney, J. Inorg. Nucl. Chem., 30, 839 (1968).
110. "Sadtlér Standard Spectra", Sadtlér Research Laboratories, 1965, #9197.
111. S.J. Cristol, K.R. Eilar, J. Am. Chem. Soc., 72, 4353 (1950).
112. A.M. Akena, D.S. Brown, D.G. Tuck, Can. J. Chem., 49, 1505 (1971).
113. R.T. Conley, "Infrared Spectroscopy", Allyn and Bacon, Inc., Boston, 1972, p. 187.
114. P. Vankateswarlee, J. Chem. Phys., 19, 293 (1951).