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Chemistry of Chromium Oxyfluorides and Group VIB Perfluoroglutarates

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Pure chromium oxide trifluoride was prepared for the first time by reaction of CrO_3 and ClF, with subsequent multiple fluorine treatments at 120°C. On the basis of its infrared spectrum, the purple $CrOF_3$ was assigned as a fluorine-bridged polymer with terminal oxygen groups. Chromium oxide trifluoride was found to be stable to 300°C, where it decomposes with the loss of oxygen to CrF_3.

A limited study of the reaction chemistry of $CrOF_3$ was carried out. With the Lewis bases, KF and NO_2F, $CrOF_3$ was found to form 1:1 adducts. The x-ray powder pattern of the KF adduct matched literature values for $KCrOF_4$. Infrared spectral data for $KCrOF_4$ indicates a square pyramidal structure (C_{4v} symmetry) for the $CrOF_4^-$ anion. Infrared spectral data for NO_2CrOF_4 shows that the tan solid has linear ONO^+ cations and $CrOF_4^-$ anions, with C_{4v} symmetry.

Reaction of $CrOF_3$ with the strong Lewis acid, SbF_5, resulted in the loss of oxygen and formation of $CrF_2Sb_2F_{11}$. The ultraviolet spectrum of this compound in DMSO proved that chromium was present in the trivalent state and infrared spectral data supported the presence of the $Sb_2F_{11}^-$ anion.

Chromium oxide trifluoride is insoluble and unreactive with WF_6 at 110°C, but reacts with fluorine at 190°C to form CrF_5.

The anhydride $(CF_2)_3(CO)_2O$, (perfluoroglutaric anhydride), was reacted with chromium trioxide, producing the new compound $CrO_2((O_2C)_2(CF_2)_3)$, (chromyl perfluoroglutarate). The chromyl compound was also prepared by reaction of the anhydride with CrO_2F_2, and by the acid fluoride, $(FOOC(CF_2)_3COOF)$, with CrO_3. The ultraviolet spectrum of chromyl perfluoroglutarate was found to be consistent with other chromyl compounds.

Reaction of perfluoroglutaric anhydride with the other group VIB metal trioxides, MoO_3 and WO_3, resulted in 90% to 95% formation of 1:1 adducts. These new compounds were formulated, by analogy with chromyl perfluoroglutarate, as the corresponding molybdenyl and tungstenyl compounds, $MoO_2((O_2C)_2(CF_2)_3$ and $WO_2((O_2C)_2(CF_2)_3)$.

Perfluoroglutaric anhydride was also reacted with group VIB metal salts; with K_2CrO_4, addition occurred across both metal-oxygen double bonds to produce $K_2CrO_2((O_2C)_2(CF_2)_3)_2$, with Na_2MoO_4 and Na_2WO_4, addition across only one metal-oxygen double bond occurred, producing $Na_2MoO_3((O_2C)_2(CF_2)_3)$ and $Na_2WO_3((O_2C)_2(CF_2)_3)$.

Infrared spectra of all the perfluoroglutarate compounds indicated unidentate carboxylate linkage to the metal. X-ray data and the results of elemental analysis are also reported.

New preparative routes to chromium oxide tetrafluoride were sought; all new methods failed to produce $CrOF_4$. Chromium oxide tetrafluoride was prepared by the previously reported method, and found to have terminal chromium-oxygen double bonds in the gas phase by infrared spectroscopy.

In the course of the preparation of $CrOF_4$, the little known oxyfluoride, $CrOF_2$, was prepared. Chromium oxide difluoride was assigned as a fluorine and oxygen-bridged polymer from infrared spectral data. The surface area of $CrOF_2$ was measured and reaction with F_2 at 250°C was found to produce CrF_5.

CHEMISTRY OF CHROMIUM OXYFLUORIDES AND GROUP VIB PERFLUOROGLUTARATES

by

BRUCE MICHAEL JOHNSON

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CHAPTER I

INTRODUCTION

Purpose

Hexavalent chromium compounds are strong oxidizing agents which have found use in preparative organic and inorganic chemistry. In addition, chromium compounds in higher oxidation states (V and VI) have important industrial uses, such as the preparation of polymerization catalysts and in chromium plating. Complexes of chromium with fluorinated carboxylic acids and alcohols have been used to waterproof fabrics and shrinkproof wool.

To expand the chemistry of chromium in high oxidation states, it is of interest to increase the number of available compounds. Work was extended on the stabilization of hexavalent chromium by preparing a new chromyl compound with a bidentate, fluorinated dicarboxylate ligand. Also new salts of the unusual pentavalent oxidation state of chromium were prepared.

Transition Metal Perfluoroglutarate Complexes

Despite well founded criticism (1), fluorine containing organic compounds are generally named after their hydrocarbon analogues by adding the prefix "fluoro". The prefix "perfluoro" is used with a compound's common name to indicate the substitution of all non-functional group hydrogens with fluorine.

Hence, perfluoroglutaric acid is used as the common name for 2,2,3,3,4,4-hexafluoropentanedioic acid.

The substitution of fluorine for hydrogen in organic compounds markedly changes their properties. The large increase in molecular weight is not accompanied by increases in melting or boiling points, which indicates a decrease in intermolecular bonding forces. In fact, when the boiling points of fluorocarbons are plotted against their molecular weights, the resulting curve lies not far above the curve for the inert gases (2). Thus, glutaric acid (MW=132 g/mole) melts at 97.5°C yet perfluoroglutaric acid (MW=240 g/mole) melts at 88°C. Even more striking is perfluoroglutaric anhydride which boils at 72°C, 208°C lower than the boiling point of glutaric anhydride, but this last example also reflects the result of the loss of hydrogen bonding.

Fluorocarbon groups are more resistant to oxidation than the corresponding hydrocarbons. Chromyl acetate, $CrO_2(O_2CCH_3)_2$, is explosive at room temperature (3) yet chromyl trifluoroacetate, $CrO_2(O_2CCF_3)_2$, melts at 48.5 ± 1°C (4). This stability results from the greater strength of the carbon-fluorine bond and the presence of the lone electron pairs on fluorine which extend far enough to shield the carbon backbone from electrophilic attack but not so far as to sterically hinder one another, which is the case in polychlorinated compounds.

Perfluorination of organic acids increases their acid strength by the inductive effect of fluorine stabilizing the conjugate base. This electronic effect also causes changes in infrared spectra. The highest frequency carbonyl stretching mode of perfluoroglutaric anhydride occurs at 1878 cm^{-1}, which is blue shifted 50 cm^{-1} relative to the hydrogen analogue. This stretching frequency is at the extreme upper limit for this functional group. The fluorine inductive effect possibly increases the carbonyl bond force constant by encouraging the shift of electron density from the lone pairs on oxygen to the bonding system, causing triple bond-like behavior.

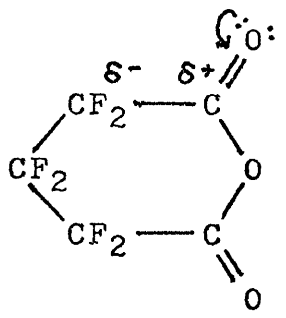


Figure 1. Fluorine inductive effect on the carbonyl groups of perfluoroglutaric anhydride.

A variety of metal-glutarate complexes have been prepared but not well characterized (5, 6). Very few perfluoroglutarate complexes have been reported. In a solubility study, Amaral and de Carvalho (7) prepared the glutarates and some perfluoroglutarates of the rare earth elements by refluxing the metal oxide and acid in aqueous solution, then crystallizing under vacuum. Using this method, the following perfluoroglutarate complexes were prepared:

I-1 $La_2O_3 + 3PFGA \xrightarrow[H_2O]{100^{\circ}C} La_2(PFG)_3 \cdot 7H_2O$

I-2 $Nd_2O_3 + 3PFGA \longrightarrow Nd_2(PFG)_3 \cdot 4H_2O$

I-3 $Gd_2O_3 + 3PFGA \longrightarrow Gd_2(PFG)_3 \cdot xH_2O$

I-4 $Dy_2O_3 + 3PFGA \longrightarrow Dy_2(PFG)_3 \cdot xH_2O$

I-5 $Er_2O_3 + 3PFGA \longrightarrow Er_2(PFG)_3 \cdot 8H_2O$

I-6 $Tm_2O_3 + 3PFGA \longrightarrow Tm_2(PFG)_3 \cdot xH_2O$

I-7 $Yb_2O_3 + 3PFGA \longrightarrow Yb_2(PFG)_3 \cdot xH_2O$

(PFGA = perfluoroglutaric acid)
(PFG = perfluoroglutarate)

The perfluoroglutarate complexes were found to be very hygroscopic and had solubilities roughly three orders of magnitude greater than their hydrocarbon analogues. No other physical or structural data was given.

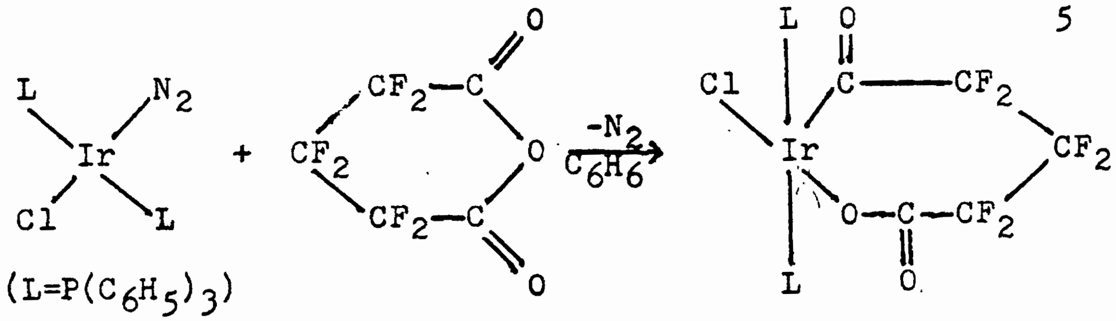
A mercury complex has also been prepared (8) by reacting mercuric oxide and perfluoroglutaryl chloride in aqueous solution:

I-8 $HgO + PFGCl \xrightarrow{H_2O} \xrightarrow{evac.} HgPFG \cdot xH_2O$

Again, no structural data was given but the reported mass balance suggests some water of crystallization.

The only other report of a perfluoroglutarate complex is by Blake et al. (9) who carried out the reaction in a strictly anhydrous, closed system. Oxidative addition of perfluoroglutaric anhydride to an iridium (I) complex occurred with ring opening to produce a bifunctional ligand with acyl and unidentate carboxylate linkages:

I-9



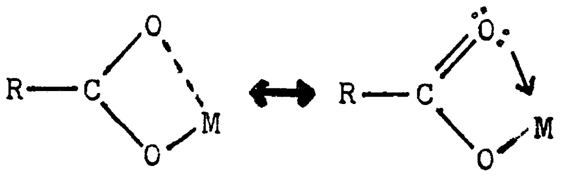
The structure was supported with infrared spectral data but the complex was presumed to contain a seven-membered chelate ring instead of polymeric chains.

Figure 2 illustrates the linkage isomerism of carboxylate groups. Because of low symmetry and vibrational coupling, along with differences in the metal's ionic radius, oxidation state, other bound groups, etc., the number and position of infrared bands do not provide a general distinction between the modes of carboxylate coordination.

Unidentate coordination leaves one of the carbon-oxygen bonds with enhanced double bond character (10) and the stretching frequencies correspond to approximately C=O and C-O (11). Despite the formal valence bond structures, investigators assign carbon-oxygen stretching frequencies in unidentate carboxylate complexes as asymmetric and symmetric CO_2 (9-16). This reflects the strong electronic interaction that is believed to occur between the three atoms of the carboxylate group. The relatively large separation between the asymmetric and symmetric CO_2 stretching frequencies is used to distinguish between unidentate carboxylate and the other various bidentate forms. In studies where the absolute configurations were confirmed by x-ray data (11, 14), $\Delta\omega$

I. Unidentate

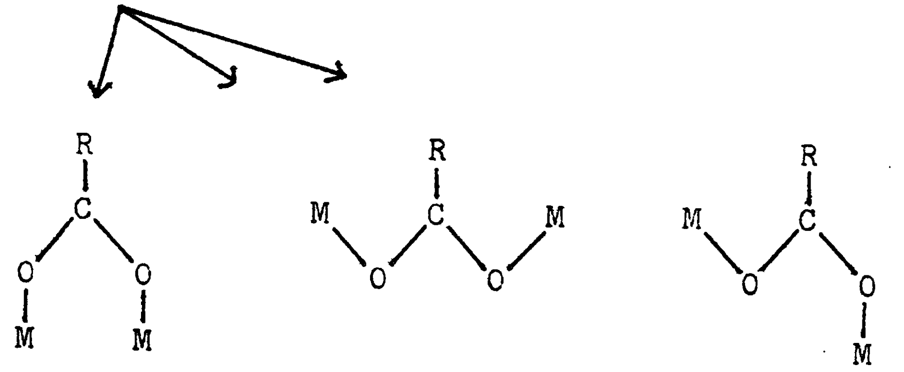
II. Bidentate - symmetrical chelate



III. Bidentate - unsymmetrical chelate

IV. Bidentate - bridging (syn - syn)

V. Ionic



(syn - syn)

(anti - anti)

(anti - syn)

(R = alkyl group)
(M = metal)

Figure 2. Linkage isomerism of carboxylate groups.

(CO_2 asymmetric - CO_2 symmetric) was 80 to 200 cm^{-1} for bidentate carboxylates and 300 to 500 cm^{-1} for unidentate carboxylates. Robinson and Uttley (15) have proposed values of 175 to 215 cm^{-1} for bidentate, and 240 to 310 cm^{-1} for unidentate carboxylates in fluoroalkyl complexes.

Symmetrical bidentate coordination (chelating and bridging forms) leaves the two carbon-oxygen bonds somewhat equivalent and the effects on stretching frequencies are not easily predictable. Alcock et al. (11) found a slightly smaller $\Delta\omega$ for bidentate chelating with respect to bidentate bridging groups.

Bidentate unsymmetrical chelating is an uncommon mode of coordination, but Catterick and Thornton (16) suggest that unidentate coordination is the upper limit in a range of unsymmetrical chelate structures and others (11) relate the size of the metal to this effect.

Ionic carboxylate occurs in solution and in alkali metal salts. The carbon-oxygen bonds are equivalent and are of intermediate bond order. The infrared spectra of ionic carboxylates show closely separated asymmetric and symmetric CO_2 stretching frequencies about 150 to 250 cm^{-1} apart.

It should be noted that perfluoroglutaric acid is a bifunctional group ligand, therefore in addition to the various possible carboxylate linkages, the ligand as a whole can coordinate in chelating or bridging (polymeric) configurations. The preparation and properties of group VIB transition metal complexes of perfluoroglutaric acid are described in Chapter

III. The perfluoroglutarate ligand is believed to act in the bidentate bridging mode with unidentate carboxylate linkages to the metal.

Chromium Oxide Fluorides

Oxyfluorides of chromium have been prepared in oxidation states from III to VI. Although CrOCl and CrOBr are known (17, 18), apparently CrOF has not been isolated as no physical data appears in the two brief reports of its preparation. Petit and Bourlange (19) obtained CrOF by mixing Cr_2O_3 and CrF_3 in KF. Chromium oxide fluoride was also proposed to be formed in the catalytic fluorination of chlorinated hydrocarbons (20). A vaporized mixture of chlorinated hydrocarbon and aqueous HF was passed over a Cr-Al fluoride catalyst bed at 275 to 425°C. Various fluorocarbons were obtained resulting from the replacement of chlorine.

Chromium oxide difluoride ($CrOF_2$) has been prepared by Rochat, et al. (21) from the thermal decomposition of chromyl fluoride.

I-10 $CrO_2F_2 \xrightarrow{500^\circ C} CrOF_2 + \frac{1}{2}O_2$

The compound is an inert brown-black solid that is insoluble in water and common acids, bases, and organic solvents. $CrOF_2$ is stable at 1600°C in vacuo, but is converted to Cr_2O_3 when exposed to air at this temperature. The x-ray powder pattern was also reported.

Chromium oxide trifluoride ($CrOF_3$) was first prepared in impure form by Sharpe and Woolf (22) who reacted CrO_3 with

BrF_3. After evaporation of the excess BrF_3, the product retained some bromine which could not be removed, even after prolonged heating at 200°C in vacuo. It was proposed that a thermally unstable addition compound, $(BrF_2)(CrOF_4)$, was formed. Later, in an extension of this work, Clark and Sadana (23, 24) again prepared impure $CrOF_3$.

I-11 $CrF_4 + BrF_3 \xrightarrow{reflux} CrOF_3 \cdot .25BrF_3$ (23)

I-12 $CrO_3 + BrF_3 \xrightarrow{25^\circ C} CrOF_3 \cdot .25BrF_3$ (24)

I-13 $CrO_3 + BrF_5 \xrightarrow{25^\circ C} CrOF_3 \cdot .25BrF_5$ (24)

I-14 $CrO_3 + ClF_3 \xrightarrow{12^\circ C} CrOF_3 \cdot .30ClF_3$ (24)

In the first reaction (I-11) $CrOF_3 \cdot .25BrF_3$ was a by-product, probably formed through attack of the quartz system by BrF_3. Reactions I-12 to I-14 (also carried out in quartz) presumably proceed with the evolution of oxygen and either chlorine or bromine. As before, elemental analysis showed that the products were contaminated with the particular halogen fluoride and all attempts to purify them by heating in vacuum resulted in decomposition. The impure samples were dull red solids which fumed in air but had magnetic moments that demonstrated the presence of chromium(V). Attempts to obtain x-ray powder patterns failed because the silica capillaries exploded shortly after loading. This lead the authors to believe that $CrOF_3$ is unstable which is incorrect as Green (25) prepared a more pure form of $CrOF_3$ and found it to be stable up to 200°C in Pyrex glass. The preparation, characterization, and some chemistry of $CrOF_3$ is described in Chapter V.

Two oxyfluorides of chromium(VI) are known. Chromium dioxide difluoride (chromyl fluoride - CrO_2F_2) and chromium oxide tetrafluoride ($CrOF_4$). Chromyl fluoride is the most well known of the chromium oxyfluorides and a fair amount of literature exists on its properties and reaction chemistry. Engelbrecht and Grosse (26) were first to prepare pure samples of CrO_2F_2 and determine many of its physical properties. Chromium dioxide difluoride is a volatile dark violet-red solid which melts at 31.6°C to an orange-red liquid and red-brown vapor. The thermal stability of CrO_2F_2 has already been mentioned and although it is stable in the dark, it polymerizes to a white solid on exposure to ultraviolet light (21). There are many preparative routes to CrO_2F_2 which have been summarized (27), two methods appear in Chapter IV. Chromyl fluoride is a strong oxidizer which attacks glass, therefore most organic oxidations are carried out with the milder chromyl chloride. Most of the chemistry of chromyl fluoride has been with inorganic systems. A few examples are the reaction with alkali and alkaline metal fluorides forming fluorochromate salts (28):

I-15 $$2MF + CrO_2F_2 \longrightarrow M_2CrO_2F_4 \quad M = Na, K, Cs$$

I-16 $$MF_2 + CrO_2F_2 \longrightarrow MCrO_2F_4 \quad M = Ca, Mg$$

Reaction with Lewis acids to produce new chromyl compounds:

I-17 $$CrO_2F_2 + 2SO_3 \xrightarrow{25^\circ C} CrO_2(SO_3F)_2$$

I-18 $$CrO_2F_2 + TaF_5 \xrightarrow{60^\circ C} CrO_2F(TaF_6)$$

I-19 $CrO_2F_2 + SbF_5 \xrightarrow{25^\circ C} CrO_2F(SbF_6)$

I-20 $CrO_2F_2 + 2SbF_5 \xrightarrow{25^\circ C} CrO_2F(Sb_2F_{11})$

and with Lewis bases (29):

I-21 $CrO_2F_2 + NO_2F \xrightarrow{45^\circ C} NO_2CrO_2F_3$

I-22 $CrO_2F_2 + NOF \xrightarrow{25^\circ C} NOCrO_2F_3$

By comparison with chromyl fluoride, chromium oxide tetrafluoride is relatively unknown and difficult to prepare. Edwards (30) first obtained $CrOF_4$ as a by-product from the direct fluorination of chromium metal in a glass flow system. The separation of $CrOF_4$ from the other major products of the reaction was difficult and required careful fractional distillation. Chromium oxide tetrafluoride is a dark red solid which melts at 55°C to a liquid of the same color. Despite its extreme moisture sensitivity, x-ray data was obtained for the compound and it was found to have a monoclinic unit cell, $a=12.3$, $b=5.4$, $c=7.3$ Å, and $\beta=104^\circ$. Later Edwards et al. (31) prepared $CrOF_4$ by fluorination of CrO_3 in a water-cooled static system. The reaction is believed to be a stepwise replacement of fluorine for oxygen, controlled by temperature.

I-23 $CrO_3 + F_2 \xrightarrow{150^\circ C} CrO_2F_2 + \frac{1}{2}O_2$

I-24 $CrO_2F_2 + F_2 \xrightarrow{220^\circ C} CrOF_4 + \frac{1}{2}O_2$

I-25 $CrOF_4 + F_2 \xrightarrow{250^\circ C} CrF_6 + \frac{1}{2}O_2 \xrightarrow{>-100^\circ C} CrF_5 + \frac{1}{2}F_2$

At 220°C only small amounts of CrO_2F_2 were present which were pumped away from the $CrOF_4$ at -23°C. The mass spectrometric cracking pattern of $CrOF_4$ was determined and from vapor pressure measurements, thermodynamic constants were calculated.

The boiling boint of 95°C was extrapolated from the vapor pressure data as $CrOF_4$ reacts with glass, rapidly above 70°C, to produce CrO_2F_2, CrO_3, and presumably SiF_4. Like $MoOF_4$ and $ReOF_4$, $CrOF_4$ was assumed to be a cis fluorine bridged polymer with terminal oxygens.

Using the data of Edwards, and assuming C_{2v} symmetry, Russian workers calculated a theoretical infrared spectrum for $CrOF_4$ (32). Twelve fundamentals were calculated with a value of 1080 cm^{-1} for the chromium-oxygen stretching frequency. These three reports represent all that is known about $CrOF_4$ to date. Attempts to prepare $CrOF_4$ by new methods are described in Chapter IV.

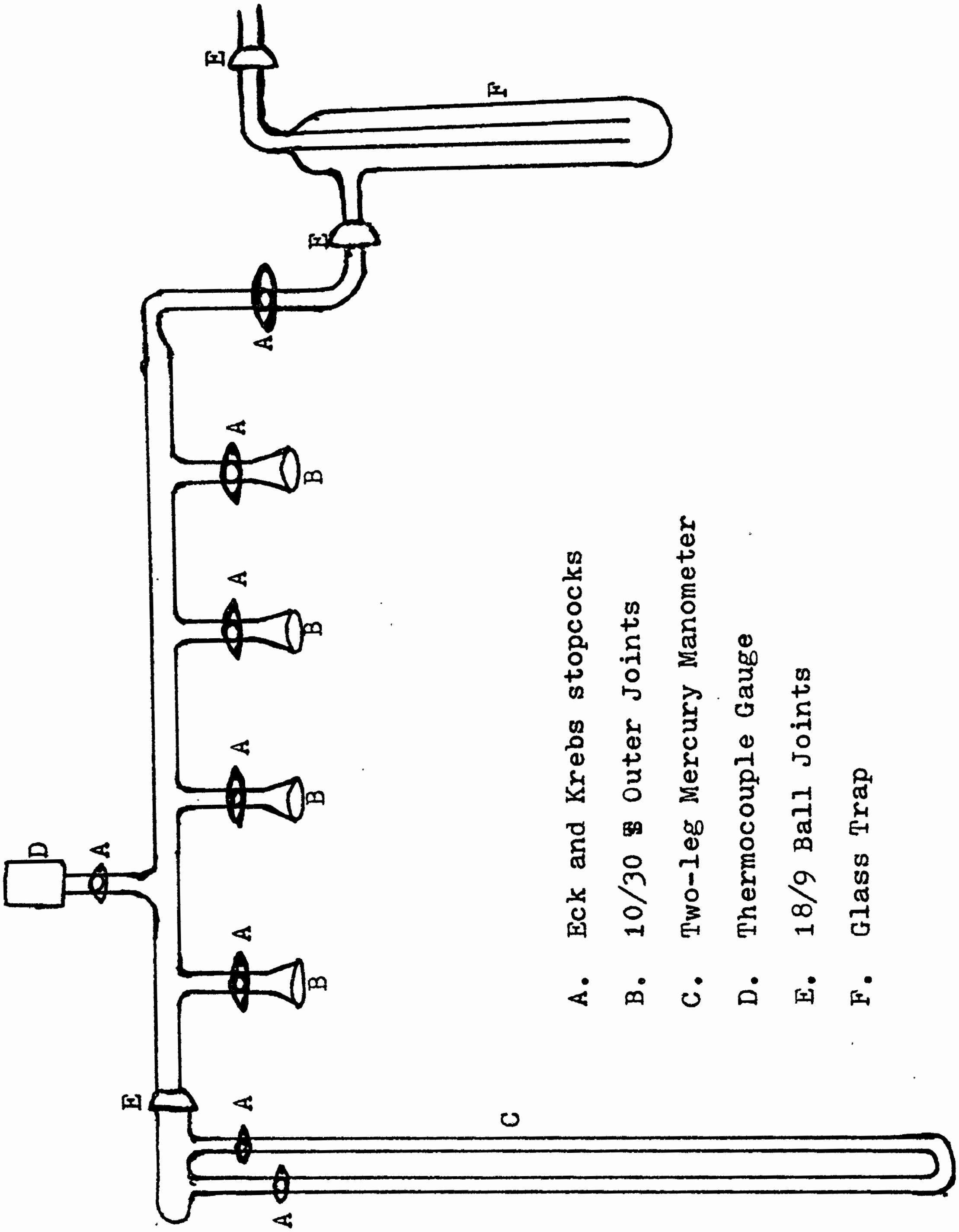
CHAPTER II

EXPERIMENTAL METHODS

Apparatus

Glass Vacuum System. For most of the work that did not involve materials reactive towards glass, the glass vacuum system was used. This consisted of a manifold evacuated through a liquid nitrogen cooled trap by a Sargent-Welch, Duo-Seal Model 1400 rotary vacuum pump. The manifold was constructed of 20 mm Pyrex glass tubing and fitted with four Eck and Krebs 2 mm high-vacuum stopcocks attached to outer 10/30 § ground glass joints. A two-leg mercury manometer, constructed of 10 mm Pyrex glass tubing was also attached to the manifold. Pressures below 1 mm Hg were monitored with a Televac thermocouple gauge. The stopcocks and ground glass joints were lubricated with Apiezon type M grease. The typical working vacuum was 5×10^{-3} to 10×10^{-3} torr. The glass vacuum manifold is illustrated in Figure 3.

Metal Vacuum System. For the transfer of extremely reactive materials used in this work, a metal vacuum line was used. The manifold was constructed of 1/4 inch O.D. copper tubing. Three taps were fitted to the manifold via Swagelok fittings. The taps consisted of a metal 10/30 § outer joint connected through a VWR stainless steel valve. The manifold was connected to a tank containing ClF and also featured a



A. Eck and Krebs stopcocks

B. 10/30 ₸ Outer Joints

C. Two-leg Mercury Manometer

D. Thermocouple Gauge

E. 18/9 Ball Joints

F. Glass Trap

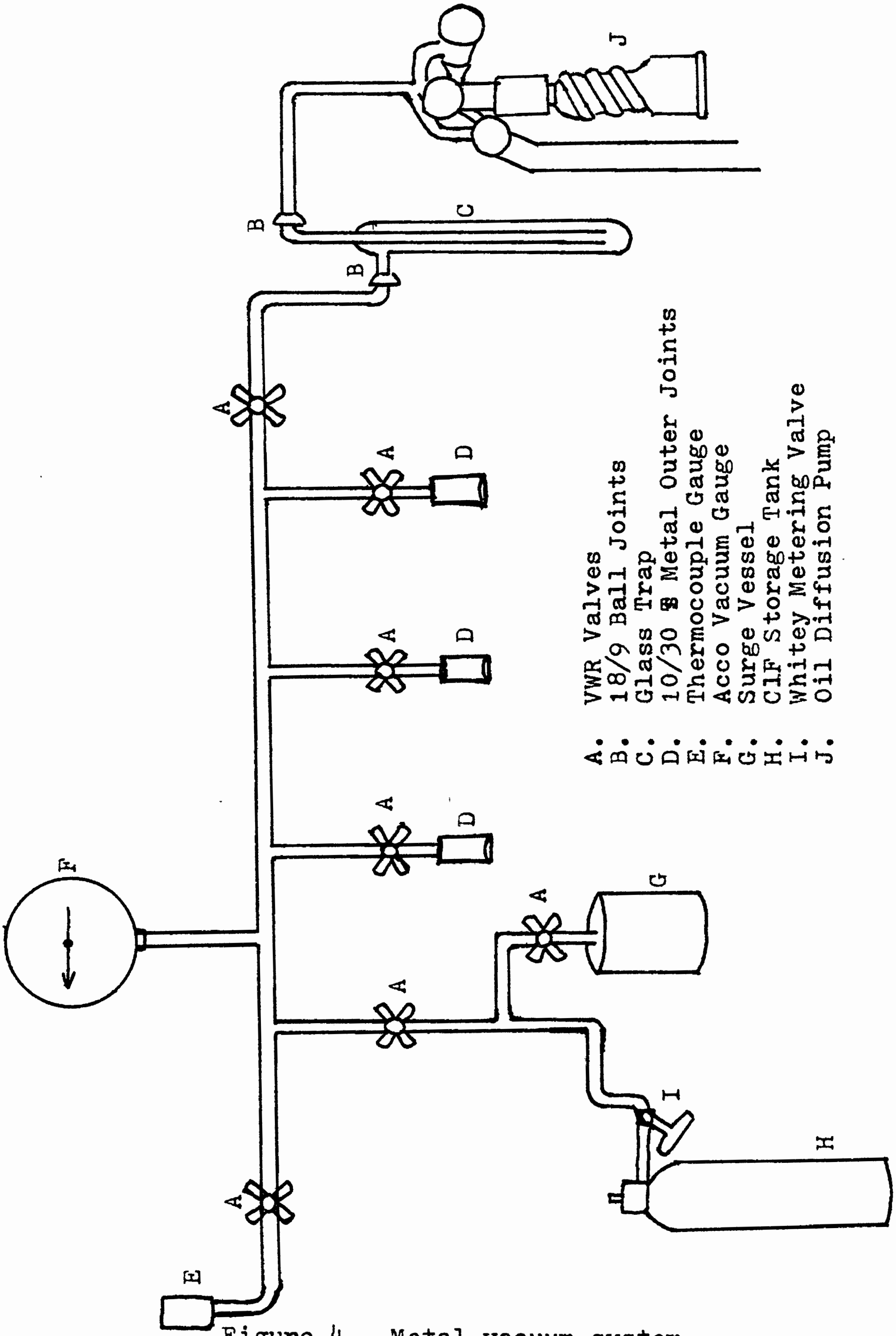
<u>Figure 3</u>. Glass vacuum manifold

1.8 liter, copper surge vessel for the metering out of gaseous reagents. The fraction of the exterior system as described above was electroless nickel plated.

An Acco diaphram type vacuum gauge was used to monitor vacuum from 1 mm to 760 mm while high vacuum was measured with a Kontes thermocouple vacuum gauge. The manifold was evacuated through a liquid nitrogen cooled trap by a pump identical to the one already described, and was equipped via a bypass system, with a CVC model VMF-10 oil diffusion pump. All ₷ joints were lubricated with Halocarbon grease. The system was capable of achieving pressures less than 10^{-3} torr with the mechanical pump alone, and is illustrated in Figure 4.

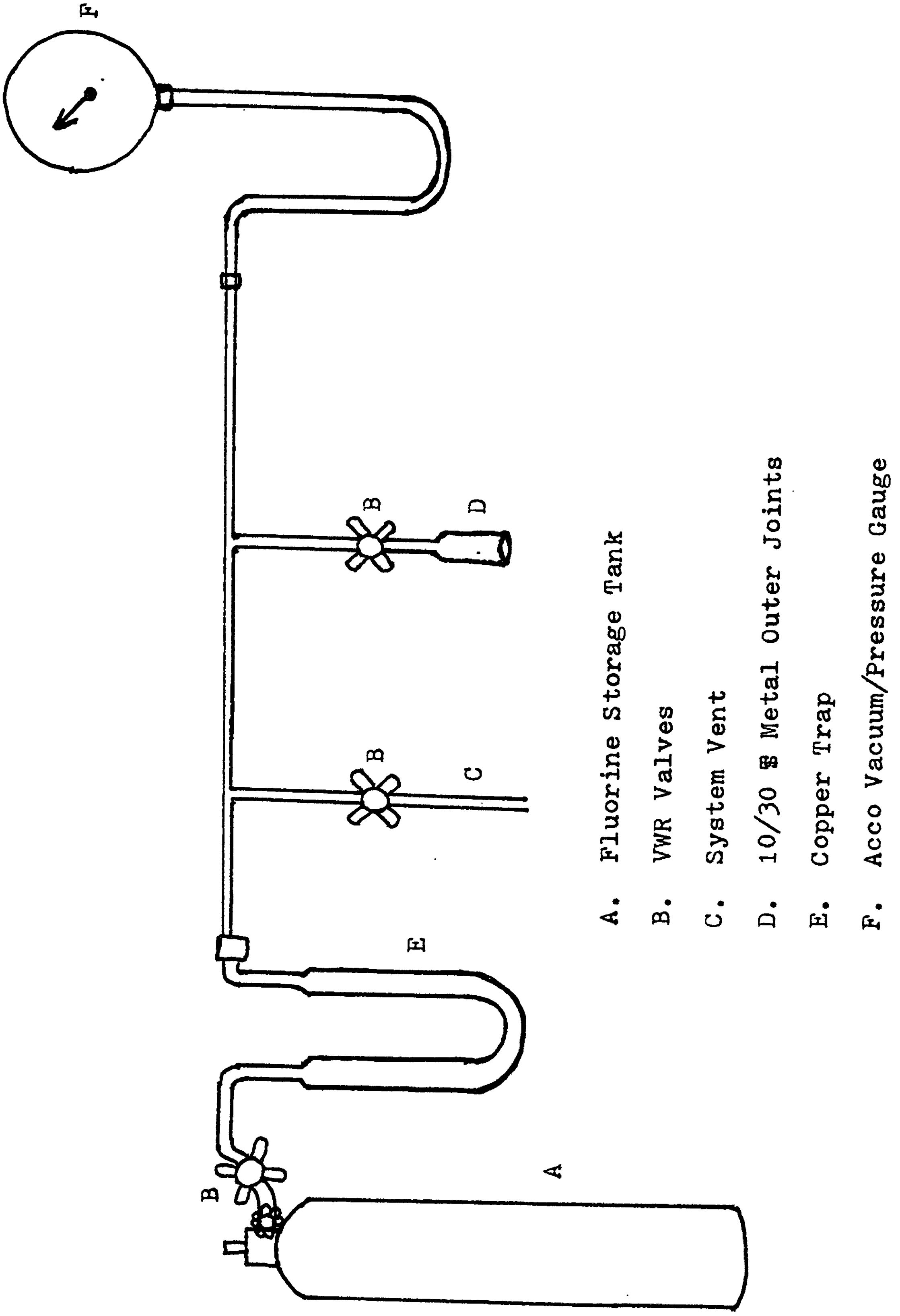
Fluorine Line. Fluorine was dispensed in a manifold constructed of 1/4 inch O.D. copper tubing to which two taps were attached. The taps consisted of brass VWR valves, one ending with a metal 10/30 ₷ outer joint and the second ending in a copper tube for use as a manifold vent. Pressure was monitored on an Acco diaphram type vacuum/pressure gauge. The manifold was connected to the fluorine tank through a copper U trap filled with nickel helices and cooled to -78°C. Halocarbon grease was used on the metal joint. The line is illustrated in Figure 5.

Vacuum Traps. For the removal of volatile materials, a glass trap was attached between the reaction vessel and the vacuum manifold. A typical trap consisted of an outer



A. VWR Valves
B. 18/9 Ball Joints
C. Glass Trap
D. 10/30 ₮ Metal Outer Joints
E. Thermocouple Gauge
F. Acco Vacuum Gauge
G. Surge Vessel
H. ClF Storage Tank
I. Whitey Metering Valve
J. Oil Diffusion Pump

Figure 4. Metal vacuum system



A. Fluorine Storage Tank
B. VWR Valves
C. System Vent
D. 10/30 ₸ Metal Outer Joints
E. Copper Trap
F. Acco Vacuum/Pressure Gauge

Figure 5. Fluorine line

tube of 20 mm I.D. Pyrex glass, to which a Kontes high vacuum Teflon valve was attached by 8 mm Pyrex tubing, and an inner tube of 8 mm I.D. Pyrex glass ending in another Teflon valve. Both valves were tipped with 10/30 \$ ground glass joints. A trap is illustrated in Figure 6.

<u>Reaction Vessels</u>. Reaction vessels were composed of either Pyrex glass, fused silica, stainless steel, Monel, or Inconel. The Pyrex glass vessels were constructed from a 100 ml round bottom flask to which had been sealed a Kontes high vacuum Teflon valve fitted with an inner 10/30 \$ ground glass joint. The fused silica vessels were similarly outfitted but the body of the vessel was cylindrical, being constructed of 22, 40, or 50 mm tubing resulting in a vessel volume of 30, 70, or 100 ml, respectively. The body of the vessel was attached to the valve through a graded seal. The Pyrex glass and fused silica vessels were equipped with Teflon coated stirring bars.

Hoke stainless steel cylinders were used for reactions involving pressures up to 100 atmospheres. The vessels had a volume of 75 ml and were equipped with either Hoke, Whitey, or VWR stainless steel valves attached to metal 10/30 \$ inner joints.

High pressure reactions up to 300 atmospheres were run in a 100 ml Hoke Monel cylinder equipped with a Hoke high pressure stainless steel metering valve attached to a metal 10/30 \$ inner joint.

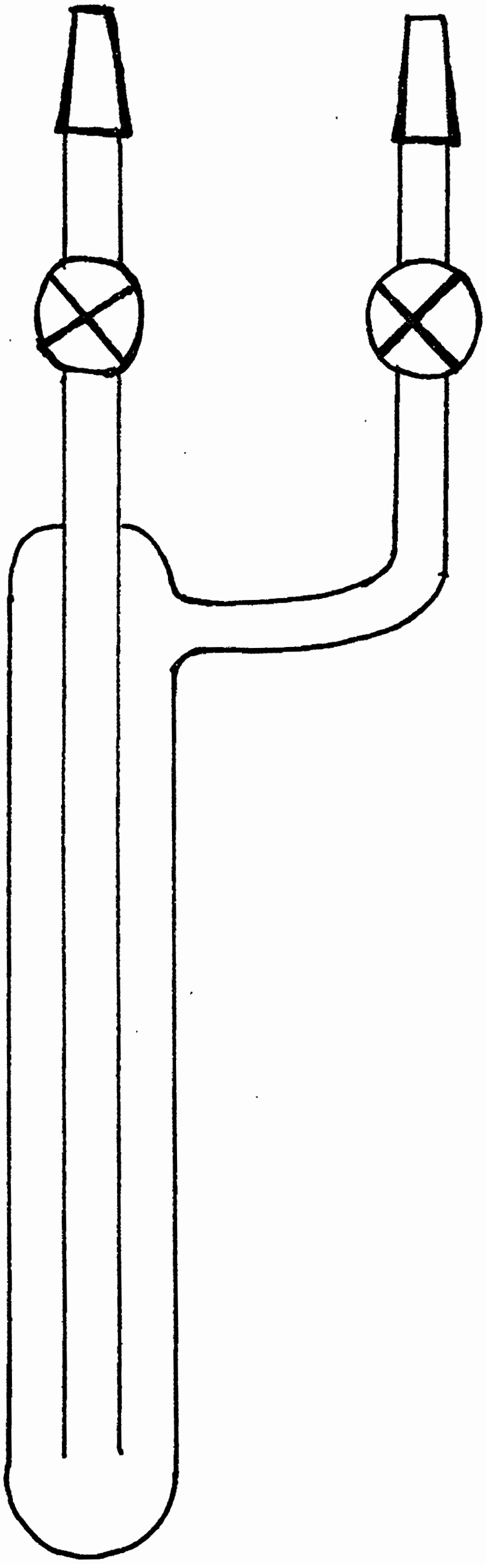


Figure 6. Glass trap

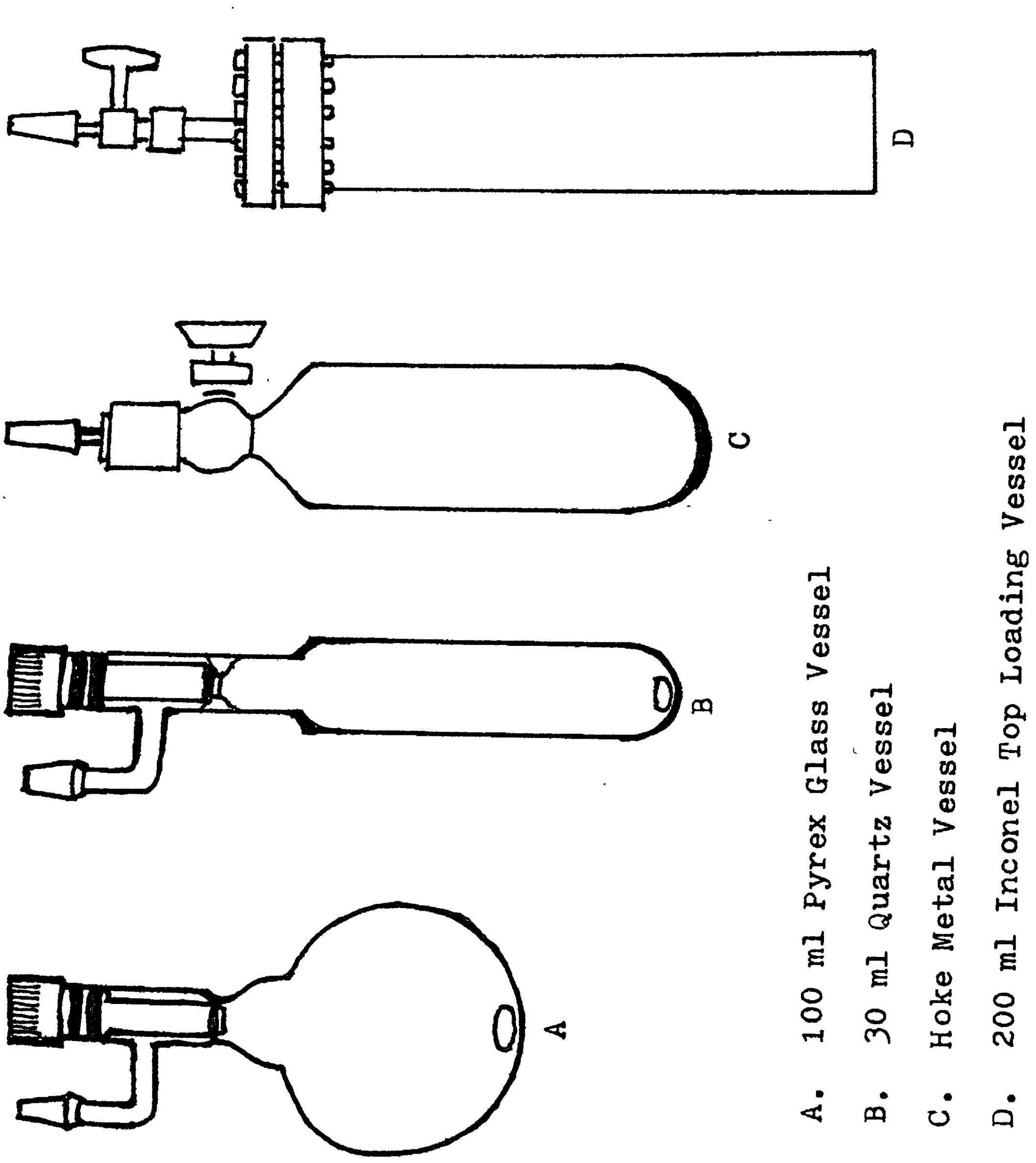
The reaction of chromium trioxide with elemental fluorine was carried out in a 200 ml top loading Inconel vessel. The lid was secured with a lead gasket and twelve 3/8 inch bolts. The vessel was equipped with a Whitey stainless steel metering valve fitted to an inner 10/30 \$ metal joint.

Metal vessels were passivated before reactions were run by heating them while they contained either chlorine monofluoride (ClF) or fluorine (F_2). Frequently nickel bushings 6 mm in diameter were added to the vessels to facilitate mixing of reactants. Selected reaction vessels are illustrated in Figure 7.

Dry Box. All air sensitive materials were handled in a KSE dry box. Nitrogen, used as the atmosphere, was passed through a calcium sulfate tube. A dry environment was maintained by leaving a container of phosphorous pentoxide exposed in the chamber.

Physical Methods

Infrared Spectra. Infrared spectra were recorded over the range 4000 to 250 cm^{-1} on a Perkin-Elmer 467 spectrophotometer. Gaseous samples were contained in a Monel cell with a path length of 8.25 cm. Sodium chloride or silver chloride windows were used. All surfaces that were to contact silver chloride were silver plated. The cell was equipped with a Whitey stainless steel metering valve connected to a metal 10/30 \$ inner joint. The spectra of solids were obtained either neat or as Nujol mulls between barium fluoride or



A. 100 ml Pyrex Glass Vessel
B. 30 ml Quartz Vessel
C. Hoke Metal Vessel
D. 200 ml Inconel Top Loading Vessel

Figure 7. Reaction vessels

KRS-5 plates, or as potassium bromide pellets. The pellet die and KBr (Mallinckrodt, Infrared Grade) were taken directly from a drying oven to the dry box, where the pellets were pressed. Infrared spectra were calibrated using polystyrene film.

Visible/Ultraviolet Spectra. Spectra were recorded in the region between 700 and 190 nm on a Cary 14 spectrometer. Cylindrical quartz sample cells with a path length of 1.0 cm were used.

X-ray Powder Spectra. Powder spectra were obtained with a General Electric XRD-5 camera, using nickel filtered copper radiation. Pyrex or quartz capillaries of 0.5 mm diameter were used to contain the samples, which were loaded in the dry box. Exposure time varied between two and four hours. The method was calibrated by measuring the patterns of CrO_3, K_2CrO_4, and $CrF_3 \cdot 3H_2O$ which agreed with published ASTM values.

Molecular Weight Determinations. The molecular weights of vapors were determined by the vapor density method. A calibrated 200 ml Pyrex glass bulb fitted with an Eck and Krebs high vacuum Teflon valve and a glass 10/30 $ inner joint was used as the sample vessel.

Melting Points. Melting points were determined with a Mel-Temp apparatus which had a range from ambient conditions to 400°C.

Elemental Analysis. Elemental analysis of products were performed by Beller Microanalytisches Laboratorium, Gottingen, West Germany. Samples for analysis were loaded into 6 mm O.D. Pyrex glass tubes in the dry box, and flame sealed under vacuum. A sample container was fabricated out of stainless steel for the shipment of samples which were found to be reactive towards glass.

Reagents

Antimony Pentafluoride. Antimony pentafluoride (SbF_5), (Allied Chemical), was vacuum distilled from the commercial shipping cylinder to a trap containing NaF, where it was again distilled into a quartz storage vessel containing NaF. The compound was subjected to dynamic vacuum at 0°C before distillation into the reaction vessel.

Bromine Trifluoride. Bromine trifluoride (BrF_3), (Ozark-Mahoning), was condensed over NaF and then vacuum distilled into the reaction vessel.

Carbon Disulfide. Carbon disulfide (CS_2), (MC/B, Spectroquality Reagent), was used as received.

Carbon Tetrachloride. Carbon tetrachloride (CCl_4), (Mallinckrodt, SpectrAR Grade), was used as received.

Carbonyl Fluoride. Carbonyl fluoride (COF_2), (PCR), was condensed over NaF and then vacuum transferred into the reaction vessel. The infrared spectrum agreed with the literature (33).

Chlorine Monofluoride. Chlorine monofluoride (ClF), (Ozark-Mahoning), was transferred from the commercial shipping cylinder in a metal vacuum line described elsewhere. No purification was attempted. The infrared spectrum agreed with the literature (34).

Chromium Oxide Difluoride. Chromium oxide difluoride ($CrOF_2$) was prepared by the method of Rochat et al. (21) as described in Chapter IV. The compound was subjected to dynamic vacuum at 150°C before use. The x-ray powder spectrum agreed with the literature (21). An infrared spectrum appears in the Appendix.

Chromium Oxide Trifluoride. Chromium oxide trifluoride ($CrOF_3$) was prepared by a modified method from that of Green (25) as described in Chapter V. Freshly prepared $CrOF_3$ was directly transferred from the synthesis vessel to the reaction vessel in the dry box, then subjected to dynamic vacuum at 100°C. Infrared spectra appear in the Appendix.

Chromium Trioxide. Chromium trioxide (CrO_3), (Baker, Reagent Grade), was transferred to the reaction vessel in the dry box, then subjected to dynamic vacuum at 150°C before use. The x-ray powder pattern matched ASTM values.

Chromyl Chloride. Chromyl chloride (CrO_2Cl_2), (Pfaltz-Bauer), was vacuum distilled from a vessel containing metallic mercury to the reaction vessel. The infrared spectrum agreed with the literature (35).

Chromyl Fluoride. Chromyl fluoride (CrO_2F_2) was prepared by two methods developed by Green and Gard (27) and is described in Chapter IV. The compound was subjected to dynamic vacuum at -78°C before sublimation through the metal vacuum line to the reaction vessel. The infrared spectrum agreed with the literature (36) and appears in the Appendix.

Dimethyl Sulfoxide. Dimethyl sulfoxide ($(CH_3)_2SO$), (MC/B, Spectroquality Reagent), was used as received.

Fluorine. Fluorine (F_2), (Air Products, 98%), was passed through a copper trap filled with nickel helices, cooled to -78°C, in a metal line described elsewhere.

Hydrogen Fluoride. Hydrogen fluoride (HF), (Matheson), was distilled into the reaction vessel through the metal vacuum line. The infrared spectrum agreed with the literature (37) with no extraneous bands present.

Molybdenum Trioxide. Molybdenum trioxide (MoO_3), (MC/B, Reagent Grade), was transferred to the reaction vessel in the dry box, then subjected to dynamic vacuum at 150°C before use. The x-ray powder pattern matched ASTM values.

Nitryl Fluoride. Nitryl fluoride (NO_2F), (Ozark-Mahoning), was found to be highly contaminated with NO_2 and N_2O_4. The commercial shipping cylinder was cooled to -78°C and then crude NO_2F was distilled through the metal vacuum line to a metal vessel containing NaF. The metal vessel was now held at -78°C and pure NO_2F was vacuum distilled directly into the reaction vessel. The infrared spectrum agreed with the literature (38).

Perfluoroglutaric Anhydride. Perfluoroglutaric anhydride ($(CF_2)_3(CO)_2O$), (PCR), was vacuum distilled directly into the reaction vessel. The infrared spectrum agreed with the literature (39).

Perfluoroglutaryl Fluoride. Perfluoroglutaryl fluoride ($(CF_2)_3(COF)_2$), (PCR), was handled in the same manner as the anhydride.

Potassium Chromate. Potassium chromate (K_2CrO_4), (Mallinckrodt, Reagent Grade), was subjected to dynamic vacuum while heating at 150°C before use.

Potassium Fluoride. Potassium fluoride (KF), (Baker, Anhydrous Reagent), was transferred to the reaction vessel in the dry box, then subjected to dynamic vacuum.

Sodium Molybdate Dihydrate. Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$), (Mallinckrodt, Reagent Grade), was dehydrated by heating in vacuo at 140°C until a high vacuum was achieved. The x-ray powder pattern matched ASTM values for Na_2MoO_4.

Sodium Perfluoroglutarate. Sodium perfluoroglutarate ($Na_2(O_2C)_2(CF_2)_3$) was prepared by hydrolyzing the anhydride (PCR) and titrating the resulting acid solution with sodium hydroxide (Mallinckrodt, Reagent Grade) to a pH 7 endpoint. The salt solution was evaporated, then subjected to dynamic vacuum at 20°C. The white crystals of sodium perfluoroglutarate were mildly hygroscopic and decomposed above 280°C. An infrared spectrum appears in the Appendix.

Sodium Tungstate Dihydrate. Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), (Mallinckrodt, Reagent Grade), was treated in the same manner as the molybdenum salt. The x-ray powder pattern matched ASTM values for Na_2WO_4.

Trifluoroacetic Acid. Trifluoroacetic acid (CF_3COOH), (PCR), was contacted with P_4O_{10} then vacuum distilled into the reaction vessel.

Tungsten Hexafluoride. Tungsten hexafluoride (WF_6), (Ozark-Mahoning), was vacuum distilled onto NaF, then redistilled into the reaction vessel. The infrared spectrum agreed with the literature (40).

Tungsten Trioxide. Tungsten trioxide (WO_3), (MC/B, Reagent Grade), was transferred to the reaction vessel in the dry box, then subjected to dynamic vacuum at 150°C before use. The x-ray powder pattern matched ASTM values.

CHAPTER III

SYNTHESIS OF GROUP VI B PERFLUOROGLUTARATES

Introduction

Fluorinated acid anhydrides have been found to add across metal-oxygen multiple bonds, while the corresponding reaction with hydrocarbon anhydrides is ineffective. The proposed pathway (41) is illustrated in Figure 8. The fluoroalkyl group induces a partial positive charge on the carbonyl carbon which facilitates interaction with the π electrons in the M=O linkage. In hydrocarbon anhydrides the inductive effect is absent.

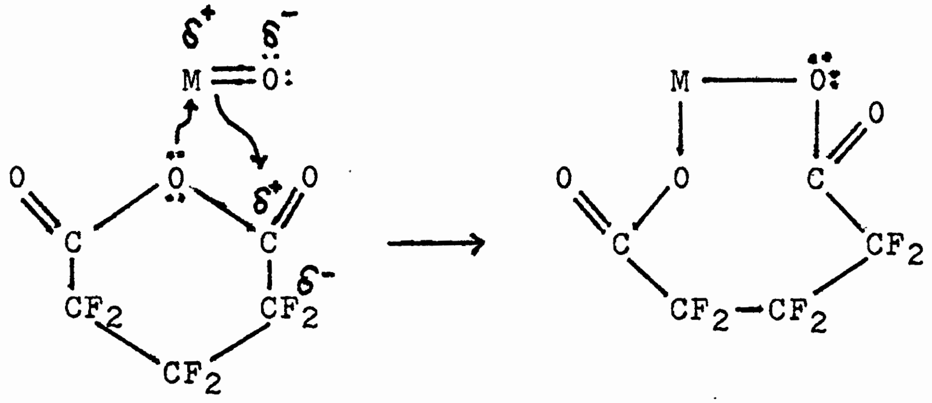


Figure 8. Proposed mechanism for the addition of acid anhydrides (perfluoroglutaric anhydride) across metal-oxygen multiple bonds.

For simplicity the figure shows a chelate structure, but a two-step mechanism would also allow a polymeric structure. In this manner, a series of chromyl compounds were prepared by reacting the appropriate acid anhydride with chromium trioxide at room temperature in the absence of light (4).

III-1 $CrO_3 + (CF_3CO)_2O \longrightarrow CrO_2(O_2CCF_3)_2$

III-2 $CrO_3 + (ClCF_2CO)_2O \longrightarrow CrO_2(O_2CCF_2Cl)_2$

III-3 $CrO_3 + (C_3F_7CO)_2O \longrightarrow CrO_2(O_2CC_3F_7)_2$

The products were shown to have unidentate carboxylate linkages by their infrared spectra which is in accord with the four coordinate, tetrahedral structure of chromyl compounds. The products were also soluble in carbon tetrachloride, were moisture and light sensitive, and did not explode with handling or heating above room temperature.

In addition to covalent chromyl compounds, many transition metal salts were prepared (41). A few examples are relevant to the work reported in this chapter:

III-4 $K_2CrO_4 + 2(CF_3CO)_2O \xrightarrow[\text{1 day}]{25^\circ C} K_2CrO_2(O_2CCF_3)_4$

III-5 $Na_2MoO_4 + 2(CF_3CO)_2O \xrightarrow[\text{20days}]{50^\circ C} Na_2MoO_2(O_2CCF_3)_4$

III-6 $Na_2WO_4 + 2(CF_3CO)_2O \xrightarrow[\text{7 days}]{50^\circ C} Na_2WO_2(O_2CCF_3)_4$

Based on the above work, it was thought that a chromyl compound containing a bivalent ligand in place of the customary two univalent ligands, might exhibit interesting properties such as increased stability. A new chromyl compound, chromyl perfluoroglutarate, was prepared by reacting chromium trioxide with perfluoroglutaric anhydride:

III-7 $CrO_3 + (CF_2)_3(CO)_2O \xrightarrow[\text{5 days}]{35^\circ C} CrO_2((O_2C)_2(CF_2)_3)$

Chromyl perfluoroglutarate was also prepared by two other methods:

III-8 $2CrO_3+FOC(CF_2)_3COF \xrightarrow[2\ \text{days}]{30^\circ C} CrO_2((O_2C)_2(CF_2)_3)+CrO_2F_2$

III-9 $CrO_2F_2+2(CF_2)_3(CO)_2O \xrightarrow[1\ \text{day}]{0^\circ C} CrO_2((O_2C)_2(CF_2)_3)+FOC(CF_2)_3COF$

In addition, the analogous molybdenyl and tungstenyl compounds were prepared:

III-10 $MoO_3+(CF_2)_3(CO)_2O \xrightarrow[13\ \text{days}]{60^\circ C} MoO_2((O_2C)_2(CF_2)_3)$

III-11 $WO_3+(CF_2)_3(CO)_2O \xrightarrow[50\ \text{days}]{80^\circ C} WO_2((O_2C)_2(CF_2)_3)$

Group VI B perfluoroglutarate salts were prepared in reactions similar to those already described (equations III-4, III-5, III-6) except that in the case of the molybdenum and tungsten salts, addition occurred across only one metal-oxygen double bond:

III-12 $K_2CrO_4+2(CF_2)_3(CO)_2O \xrightarrow[24\ \text{days}]{50^\circ C} K_2CrO_2((O_2C)_2(CF_2)_3)_2$

III-13 $Na_2MoO_4+(CF_2)_3(CO)_2O \xrightarrow[13\ \text{days}]{55^\circ C} Na_2MoO_2((O_2C)_2(CF_2)_3)$

III-14 $Na_2WO_4+(CF_2)_3(CO)_2O \xrightarrow[19\ \text{days}]{50^\circ C} Na_2WO_2((O_2C)_2(CF_2)_3)$

Perfluoroglutaric anhydride appears to be less reactive than trifluoroacetic anhydride in the addition across metal-oxygen double bonds. This is clearly reflected in the temperature and time required for analogous reactions. The cyclic structure of perfluoroglutaric anhydride is probably responsible for this effect. Perfluoroglutarate compounds are also relatively unstable when compared to the trifluoroacetate compounds. The longer fluorocarbon chain and the presence of the less shielded $-CF_2-$ group may be the cause of this instability as chromyl perfluorobutyrate ($CrO_2(O_2CC_3F_7)_2$) was also found to be unstable, decomposing at room temperature (4).

Physical and structural data for the perfluoroglutarate compounds appear in the experimental and discussion sections.

Experimental

Reaction of Chromium Trioxide With Perfluoroglutaric Anhydride. Chromium trioxide (8.58 mmoles) was added to a thoroughly dried 100 ml Pyrex glass vessel. Perfluoroglutaric anhydride (112 mmoles) was then condensed into the vessel via vacuum distillation. The reaction mixture was protected from light, and heated with stirring at 35°C for 5 days. The violet crystals of CrO_3 slowly turned to a red-brown powder while the liquid organic anhydride phase remained clear. Upon evacuation of the vessel at 0°C, through a trap cooled with liquid nitrogen, no non-condensable gases were found. After removal of the excess anhydride, the vessel was found to contain a slightly volatile tan-brown powder. The weight pickup of the vessel corresponded to 8.49 mmoles of perfluoroglutaric anhydride, 99% of that expected for 1:1 stoichiometry. Analysis for $CrO_2((O_2C)_2(CF_2)_3)$ (chromyl perfluoroglutarate)- Cr; Requires: 16.15% Found: 17.67%, C; Requires: 18.65% Found: 17.01%, F; Requires: 35.4% Found: 35.1%. The product is very hygroscopic, hydrolyzing to a yellow chromic acid solution according to the equation:

III-15 $CrO_2((O_2C)_2(CF_2)_3)+2H_2O \longrightarrow CrO_4^{=}+{}^{-}OOC(CF_2)_3COO^{-}+4H^{+}$

Based on this equation, the compound was analyzed for chromium in this laboratory by iodometric and acid/base titration.

Analysis for $CrO_2((O_2C)_2(CF_2)_3)$ - Requires: Cr, 16.15% Found: Cr, 15.6% via iodometry, 16.1% via acidity.

Chromyl perfluoroglutarate is a strong oxidizer which ignites acetone and methanol, oxidizes CH_3CN, is insoluble in CS_2 and perfluoroalkane -70, and is only very slightly soluble in CCl_4 forming a brown solution. An ultraviolet spectrum of the product in CCl_4 showed two absorbtions, one at 274 nm and a weaker transition at 408 nm.

An attempt was made to purify the product via vacuum sublimation. From ambient temperature to 60°C, very small amounts of an orange-brown solid condensed in the cold trap. Near 85°C a violent explosion occurred producing CO_2, COF_2, and CF_3COF among other products, as identified by their respective infrared spectra (42, 33, 43). When the product is slowly heated in a sealed glass capillary, decomposition occurs above 80°C, rapid heating results in explosive decomposition around 70°C to 90°C.

The x-ray diffraction powder pattern of the product is listed in Table I. An infrared spectrum is listed in Table II and also appears in the appendix.

<u>Reaction of Chromium Trioxide With Perfluoroglutaryl Fluoride</u>. Perfluoroglutaryl fluoride (75.5 mmoles) was vacuum distilled into a 100 ml quartz vessel containing 7.87 mmoles of CrO_3. The mixture was heated with stirring in the dark at 30°C. After 20 hours red-brown vapors started to form which were periodically removed from the vessel by brief

TABLE I

X-RAY POWDER PATTERN OF CHROMYL PERFLUOROGLUTARATE

d (Å)	Intensity	d (Å)	Intensity
13.89	w	3.43	s
11.21	vw	3.29	vw
11.13	m	3.10	vw
9.24	vw	2.98	vw
8.37	w	2.87	m
7.54	w	2.62	vw
6.51	w	2.47	vw
5.85	vw	2.39	vw
5.69	vw	2.34	vw
5.47	vw	2.25	vw
4.95	m	2.23	vw
4.73	vw	2.19	w
4.55	m	1.92	vw
4.18	s	1.82	vw
3.99	vw	1.74	vw
3.84	m	1.50	vw

s = strong
m = medium
w = weak
vw = very weak

TABLE II

INFRARED SPECTRA OF CHROMYL PERFLUOROGLUTARATE IN CM^{-1}

(A) $CrO_3+(CF_2)_3(CO)_2O \longrightarrow CrO_2((O_2C)_2(CF_2)_3)$

(B) $2CrO_3+FOC(CF_2)_3COF \longrightarrow CrO_2((O_2C)_2(CF_2)_3)+CrO_2F_2$

(C) $CrO_2F_2+2(CF_2)_3(CO)_2O \longrightarrow CrO_2((O_2C)_2(CF_2)_3)+FOC(CF_2)_3COF$

A	B	C	Assignment
	3740 w	3745 w	impurity
	1875 m	1880 m	impurity
1780 s	1755 s	1760 s	ν (asym CO_2)
1655 s,b	1630 s,b	1630 s,b	ν (asym CO_2) $\Delta\omega$ =365
1415 m,b	1418 s	1425 s	ν (sym CO_2)
1255 m	1265 m	1260 m	ν (C-F or sym CCO_2)
1170 vs	1150 vs	1160 vs	ν (C-F)
1055 m	1035 m	1035 m	ν (C-F)
970 s	975 s,b	975 s,b	ν (asym Cr=O)
950 s			ν (sym Cr=O)
905 m	890 m	890 m	ν (C-C)
815 m	810 s	805 m	ν (C-F)
700 s,b	680 s,b	700 s,b	δ (CCO_2)
565 m	540 m	555 m	ν (Cr-O)
325 w		310 w	and
280 w			δ (C-F)

vs = very strong
s = strong
m = medium
w = weak
b = broad

evacuation through a $^{-}196^{o}C$ trap. The red-brown vapor was identified as CrO_2F_2 by its infrared spectrum (36). The reaction appeared to be complete after 43 hours as evident by a decrease in the production of CrO_2F_2 vapors and the formation of a chocolate-brown solution. The excess acid fluoride was distilled out of the vessel at $0^{o}C$ under vacuum. A gummy brown solid remained in the vessel which slowly turned into a fine chocolate-brown powder under dynamic vacuum. The constant weight product corresponded to 4.65 mmoles of chromyl perfluoroglutarate (3.94 mmoles theoretical). Analysis for $CrO_2((O_2C)_2(CF_2)_3)$ - Cr; Requires: 16.15% Found: 12.34%, C; Requires: 18.65% Found: 20.00%, F; Requires: 35.4% Found: 43.9%.

The product was very hygroscopic, hydrolyzing to a yellow solution. Upon slow heating, the brown product slowly decomposed above $85^{o}C$. The infrared spectrum is listed in Table II.

Reaction of Chromyl Fluoride With Perfluoroglutaric Anhydride. Perfluoroglutaric anhydride (18.7 mmoles) and chromyl fluoride (5.36 mmoles) were vacuum distilled into a 100 ml quartz vessel and stirred at $0^{o}C$ in the dark. After 25 hours, all red-brown vapors of CrO_2F_2 had disappeared and the solution had gone from orange to dark brown in color. An infrared spectrum of the vapors showed the presence of perfluoroglutaryl fluoride.

The vessel was evacuated at $0^{o}C$. A small amount of tan-brown solids sublimated out of the vessel. The material remaining in the vessel reduced to a sticky dark brown semisolid. Pumping on the vessel to constant weight resulted in the recovery of a dark brown powder. The weight of the product corresponded to 5.34 mmoles of chromyl perfluoroglutarate. Analysis for $CrO_2((O_2C)_2(CF_2)_3)$ - Cr; Requires: 16.15% Found: 12.49%, C; Requires: 18.65% Found: 19.65%, F; Requires 35.4% Found: 43.6%.

The hygroscopic dark brown product hydrolyzes to a yellow solution and decomposed when heated above 60°C. The infrared spectrum is listed in Table II.

Reaction of Molybdenum Trioxide With Perfluoroglutaric Anhydride. Perfluoroglutaric anhydride (81.2 mmoles) was vacuum distilled into a 100 ml Pyrex glass vessel containing 2.7 mmoles of predried molybdenum trioxide. After 9 days at 60°C the reaction mixture had a slight blue tint, indicating reduced states of molybdenum. The excess perfluoroglutaric anhydride was distilled out of the vessel after a total reaction time of 13 days.

The vessel contained a non-volatile, light blue solid which was hygroscopic and melted at 93.5°C. The weight pickup corresponded to the coordination of 2.4 mmoles of perfluoroglutaric anhydride. The infrared spectrum of the product is listed in Table III and also appears in the appendix.

Reaction of Tungsten Trioxide and Perfluoroglutaric Anhydride. To a 100 ml Pyrex glass vessel containing 4.6

TABLE III

INFRARED SPECTRA OF $MoO_2((O_2C)_2(CF_2)_3)$ AND $WO_2((O_2C)_2(CF_2)_3)$ IN CM^{-1}

$MoO_2((O_2C)_2(CF_2)_3)$	Assignment	$WO_2((O_2C)_2(CF_2)_3)$
1745 s,b	ν (asym CO_2)	1778 s,sh
	ν (asym CO_2)	1735 s,b
1410 m	ν (sym CO_2)	1420 m
	ν (C-F or sym CCO_2)	1305 w
1290 w		1280 m
1240 m		1263 m
1193 s	ν (C-F)	1190 s
1170 s	ν (C-F)	1175 s
1147 s	ν (C-F)	1160 s
1045 w	ν (C-F)	1050 w
985 m*		
845 s,b*		800 s,b*
550 s,b*		
365 m*		355 m*

*Band attributed to unreacted MoO_3 and WO_3.

s=strong
m=medium
w=weak
b=broad
sh=sharp

mmoles of predried WO_3 was added 73.5 mmoles of perfluoroglutaric anhydride via vacuum distillation. The reaction mixture was heated at 80°C with stirring for 50 days. Upon evacuation of the vessel at 20°C, a pale-yellow non-volatile solid was found which melted at 85.5°C. The weight pickup of the vessel corresponded to 4.3 mmoles of perfluoroglutaric anhydride. Analysis for $WO_2((O_2C)_2(CF_2)_3)$ - C; Requires: 13.22% Found: 10.08%, W; Requires: 40.51% Found: 48.3%, F; Requires: 25.1% Found: 20.7%.

The infrared spectrum of the product is listed in Table III and appears in the appendix.

Reaction of Potassium Chromate with Perfluoroglutaric Anhydride. To 2.69 mmoles of K_2CrO_4 contained in a 100 ml Pyrex glass vessel was added 42.5 mmoles of perfluoroglutaric anhydride via vacuum distillation. The reaction mixture was stirred in the dark for 24 days at 50°C. Upon evacuation of the vessel at 20°C a green solid was found. The weight gain of the vessel corresponded to 5.42 mmoles of the anhydride or a stoichiometry of 2:1 anhydride to salt. Analysis for $K_2CrO_2((O_2C)_2(CF_2)_3)_2$ - Cr; Requires: 8.2% Found: 9.8%, C; Requires: 18.80% Found: 16.95%, F; Requires 35.7% Found: 33.0%.

The product was hygroscopic, hydrolyzing to a yellow solution, and melted at 150°C. A unique x-ray powder pattern was obtained in which only the two strongest lines for K_2CrO_4 appear as medium intensity lines. The x-ray powder pattern is listed in Table IV and the infrared spectrum is listed in Table V and appears in the appendix.

TABLE IV

X-RAY POWDER PATTERN OF $K_2CrO_2((O_2C)_2(CF_2)_3)_2$

d (Å)	Intensity	d (Å)	Intensity
19.53	m	3.23	w
8.34	w	3.08	m*
7.52	m	2.98	m*
6.20	m	2.91	vw
5.53	s	2.84	w
5.29	vs	2.75	w
5.16	vs	2.71	vw
4.96	w	2.64	vw
4.76	w	2.57	m
4.62	s	2.47	w
4.31	s	2.40	vw
4.16	w	2.34	vw
3.88	s	2.30	m
3.73	w	2.23	vw
3.41	w	2.14	w
3.30	w		

*K_2CrO_4 impurity

s=strong
vs=very strong
m=medium
w=weak
vw=very weak

TABLE V

INFRARED SPECTRUM OF $K_2CrO_2((O_2C)_2(CF_2)_3)_2$ IN CM^{-1}

$K_2Cr_2O_2((O_2C)_2(CF_2)_3)_2$	Assignment
1780 s	ν (asym CO_2)
1650 m,b	ν (asym CO_2)
1430 m,b	ν (sym CO_2)
1325 w	ν (sym CCO_2)
1283 w	ν (sym CCO_2)
1262 m	ν (C-F or sym CCO_2)
1180 s,b	ν (C-F)
1155 s	ν (C-F)
1051 m	ν (C-F)
957 m	ν (Cr-O-C)
919 w	
894 m	ν (C-C)
818 w	ν (C-F)
789 w	
757 w	
737 w	δ (CCO_2)
630 w	δ (CCO_2)

s=strong
vs=very strong
m=medium
b=broad
w=weak

Reaction of Sodium Molybdate with Perfluoroglutaric Anhydride. Sodium molybdate (2.47 mmoles) and perfluoroglutaric anhydride (36.8 mmoles) were placed in a 100 ml Pyrex glass vessel and stirred at 55°C in the dark for 13 days. The excess perfluoroglutaric anhydride was removed from the vessel by evacuation at 20°C. The vessel contained a light green non-volatile solid with a weight which indicated the addition of 2.50 mmoles of perfluoroglutaric anhydride, or an apparent stoichiometry of 1:1. Analysis for $Na_2MoO_3((O_2C)_2(CF_2)_3)$ - Na; Requires: 10.7% Found: 10.8%, Mo; Requires: 22.4% Found: 21.4%, C; Requires: 14.02% Found: 13.47%, F; Requires: 26.6% Found: 26.3%.

The product was hygroscopic and decomposed above 125°C. An infrared spectrum appears in the appendix and is listed in Table VI.

Reaction of Sodium Tungstate with Perfluoroglutaric Anhydride. Perfluoroglutaric anhydride (45.9 mmoles) was vacuum distilled into a 100 ml Pyrex glass vessel containing 1.89 mmoles of Na_2WO_4. The reaction mixture was stirred in the dark for 19 days at 55°C. Upon removal of the excess anhydride, the vessel was found to contain a white solid with a weight indicating the addition of 1.92 mmoles of perfluoroglutaric anhydride. Analysis for $Na_2WO_3((O_2C)_2(CF_2)_3)$ - Na; Requires: 5.43% Found: 6.21%, W; Requires: 35.64% Found: 43.63%, C; Requires: 11.63% Found: 7.34%, F; Requires: 22.1% Found: 19.8%.

TABLE VI

INFRARED SPECTRA OF $Na_2MoO_3((O_2C)_2(CF_2)_3)$ AND $Na_2WO_3((O_2C)_2(CF_2)_3)$ IN CM^{-1}

$Na_2MoO_3((O_2C)_2(CF_2)_3)$	Assignment	$Na_2WO_3((O_2C)_2(CF_2)_3)$
1765 m	ν (asym CO_2)	1650 vs,b
1670 vs	ν (asym CO_2)	
1420 m	ν (sym CO_2)	1430 s
1400 m	ν (sym CO_2)	1410 s
1282 w	ν (sym CCO_2)	1280 m
1245 s	ν (C-F or sym CCO_2)	1245 w
1210 s	ν (C-F)	1205 w
1160 vs	ν (C-F)	1150 vs
1115 w		1125 m
1075 w		1080 w
1056 m	ν (C-F)	1050 m
945 s,b	ν (M=O?)	945 s,b
830 m	ν (C-C)	820 m
785 w		
750 m	δ (CCO_2)	745 m
630 m,b	δ (CCO_2)	
550 m	ν (Mo-O-C)	
505 m		

s=strong
vs=very strong
m=medium
b=broad
w=weak

The product melted with decomposition at 298±2 C and had a unique x-ray powder pattern which is listed in Table VII. An infrared spectrum is listed in Table VI and also appears in the appendix.

Discussion

Chromyl Perfluoroglutarate. Three synthetic routes were found to yield chromyl perfluoroglutarate. Unfortunately, common methods of purification are unsuitable for this compound as it is essentially insoluble or oxidizes, common solvents and decomposes upon attempts at vacuum sublimation.

The highest quality samples of chromyl perfluoroglutarate are a light tan to orange-brown color and come from the established method of reaction of chromium trioxide with acid anhydrides (equation III-7). Some care must be taken to isolate the product from the excess anhydride once the reaction is complete, for oxidation reactions occur with time. The reaction of chromium trioxide with perfluoroglutaric anhydride was first investigated in this laboratory by Mr. Robert Deatherage.[1]

Chromyl perfluoroglutarate appears to be slightly volatile and attempts were made to purify the initial products by vacuum sublimation at elevated temperature. The new compound, however, was found to be explosive around 80°C, producing CO_2, COF_2, and CF_3COF, among other products. This decomposition behavior was also observed for transition metal trifluoroacetates (44, 45).

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[1] Mr. Robert Deatherage, personal communication.

TABLE VII

X-RAY POWDER PATTERN OF $Na_2WO_3((O_2C)_2(CF_2)_3)$

d (Å)	Intensity	d (Å)	Intensity
5.87	m	1.95	w
5.29	s	1.90	w
4.95	w	1.86	m
3.57	w	1.79	vw
3.31	m	1.76	m
3.24	vs	1.61	m
3.06	m	1.54	m
2.92	ms	1.48	w
2.84	w	1.44	w
2.76	s	1.39	w
2.58	vw	1.35	vw
2.33	w	1.32	vw
2.27	w	1.28	vw
2.11	w	1.22	w
2.07	w	1.19	w

s=strong
vs=very strong
ms=medium strong
m=medium
w=weak
vw=very weak

The ultraviolet spectrum of chromyl perfluoroglutarate in CCl_4 (saturated solution) shows two absorbtions at 268 and and 368 nm. Similar spectra were found for other chromyl compounds which have been assigned to charge transfer transitions (46). The ultraviolet spectra of selected chromyl compounds are listed in Table VIII.

TABLE VIII

ULTRAVIOLET SPECTRA OF CHROMYL COMPOUNDS IN CCl_4

Compound	λ max (nm)		Reference
CrO_2Cl_2	298	415	46
CrO_2F_2	278	383	47
$CrO_2(O_2CCH_3)_2$	283	400	3
$CrO_2(O_2CCF_3)_2$	286	410	4
$CrO_2(O_2CCF_2Cl)_2$	281	410	4
$CrO_2(O_2CC_3F_7)_2$	278	380	4
$CrO_2((O_2C)_2(CF_2)_3)$	268	368	
$CrO_2(OSO_2F)_2$	285	360	48
$CrO_2(OSO_2CF_3)_2$	284	407	48

The infrared spectrum of chromyl perfluoroglutarate, prepared by three different methods, is listed in Table II. Spectral assignments are based largely after the work of Sharpe et al. on anhydrous transition metal trifluoroacetates (44). The asymmetric carboxylate stretching mode is widely split while symmetric carboxylate stretching shows little, or no splitting. This vibrational coupling has been observed when two carboxylate groups are bound to the same metal (49). The separation ($\Delta\omega$) between the higher frequency asymmetric CO_2 stretch and the symmetric CO_2 stretch is 365 cm^{-1}, well within the range commonly taken for unidentate carboxylate coordination (15). The absorption band around 1255 cm^{-1} is possibly due to carbon-fluorine stretching, but its position and intensity suggest that it is more likely a coupling of the symmetric CO_2 and C-C stretching modes, sometimes assigned as CCO_2 (13). Carbon-fluorine stretching is easily assigned to intense absorptions around 1150 cm^{-1}. Asymmetric and symmetric Cr=O stretching was observed at 970 and 950 cm^{-1}. In chromyl trifluoroacetate these bands were unresolved at 960 cm^{-1} (4). The remaining band assignments were made following the spectra of the trifluoroacetates.

From infrared spectral data and the insolubility in non-polar solvents, chromyl perfluoroglutarate is assumed to have a bridged (polymeric) structure with unidentate carboxylate groups.

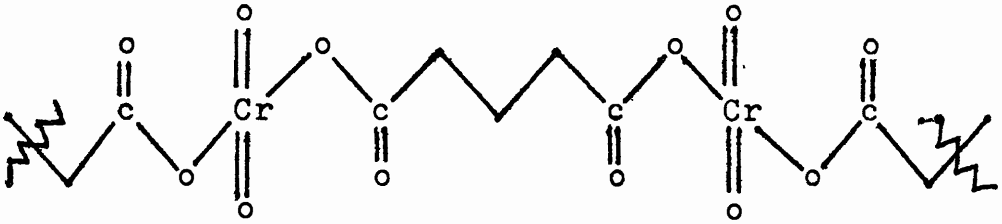

Figure 9. Proposed structure of chromyl perfluoroglutarate.

The reaction of chromium trioxide with perfluoroglutaryl fluoride (equation III-8) is similar to a previously reported preparation of chromyl fluoride:

III-16 $CrO_3+COF_2\xrightarrow{185^{\circ}C}CrO_2F_2+CO_2$ (27)

In this case, perfluoroglutaric anhydride is formed instead of the anhydride of carbonic acid (CO_2). The perfluoroglutaric anhydride thus formed reacts with CrO_3 to produce the chromyl compound.

The high weight and dark color of the sample prepared by this method indicate that the chromyl fluoride by-product oxidized a significant amount of the perfluoroglutaryl fluoride. Two impurity peaks are seen in the infrared spectrum listed in Table II, and as expected, the elemental analysis is rather poor. The high values for carbon and fluorine also indicate that oxidation products are present.

Surprisingly, the infrared spectra are in good agreement. There is a slight shifting of spectra B and C, as they were obtained as neat smears at a fast scan rate, while spectrum A is a slow scan of a KBr pellet.

The third preparative route to chromyl perfluoroglutarate, the reaction of chromyl fluoride with the anhydride (equation III-9), also is analogous to previously reported schemes. It was found that halide exchange occurred when covalent halides acted on trifluoroacetic anhydride:

III-17 $KCrO_3Cl+2(CF_3CO)_2O\longrightarrow KCrO_2(O_2CCF_3)_3+CF_3COCl$ (41)

III-18 $Cs(IF_4)+4(CF_3CO)_2O\longrightarrow Cs(I(O_2CCF_3)_4)+4CF_3COF$ (50)

III-19 $CrO_2F_2+2(CF_3CO)_2O \longrightarrow CrO_2(O_2CCF_3)_2+2CF_3COF$ (28)

Again, the presence of CrO_2F_2 caused considerable oxidation to occur, and in fact, the elemental analysis for the products from these last two methods are very similar. Overall, the preferred method for the preparation of chromyl perfluoroglutarate is the reaction of chromium trioxide with perfluoroglutaric anhydride.

Molybdenyl Perfluoroglutarate. Molybdenyl perfluoroglutarate was prepared by the same method used for the chromyl compound. Mass balance indicated that the reaction was 90% complete. Further attempts to obtain complete reactions failed, usually resulting in reduced states of molybdenum. The infrared spectrum is listed in Table III. Except for the unsplit asymmetric CO_2 stretching band, which is shifted somewhat to lower frequency, the spectrum is very similar to the other transition metal perfluoroglutarates. Spectral assignments were made, as before, with unidentate carboxylate linkage indicated.

The small amount of unreacted molybdenum trioxide obscured the low frequency region of the infrared spectrum and also dominated the x-ray powder pattern. For this reason, the x-ray data is not reported, although a few strong lines indicate the presence of a new compound and no lines were observed for any lower oxides of molybdenum.

Molybdenum blue (M_2O_5 with variations in Mo and O), resulting from mild reduction of MoO_3 (formal oxidation states between 5 and 6) has an intense blue color, therefore, this impurity is believed to be a minor one in the light blue product which was obtained.

Tungstenyl Perfluoroglutarate. After an extremely long reaction period (50 days at 80°C) tungstenyl perfluoroglutarate was prepared in 93% yield. Compared to CrO_3, WO_3 was found to be even less reactive than MoO_3 towards addition to perfluoroglutaric anhydride. Longer reaction times and somewhat higher temperatures failed to produce pure products. One problem with this reaction scheme is the absence of a solvent, either for the metal trioxide or the particular product. Anhydrous trifluoroacetic acid was tried as a possible solvent for the tungsten trioxide-perfluoroglutaric anhydride system. Unfortunately, the cyclic anhydride dehydrates the acid, a reaction that was later found to have been studied for the hydrocarbon analogues:

III-20 $$(CH_2)_3(CO)_2O + 2CH_3COOH \xrightarrow{25^\circ C} (CH_3CO)_2O + (CH_2)_3(COOH)_2 \quad K = 4.6 \cdot 10^{-1}\ M^{-1}$$ (51)

The infrared spectrum of the product is listed in Table III. Again, unidentate carboxylate linkage is indicated, and the remainder of the spectrum follows previous assignments.

Reaction of Potassium Chromate with Perfluoroglutaric Anhydride. Reaction of potassium chromate with perfluoroglutaric anhydride resulted in addition across both metal-oxygen double bonds of the salt. The infrared spectrum of the product, listed in Table IV, is almost identical to the covalent chromyl compound except that absorption bands due to Cr=O stretching are absent (52). The Cr-O-C stretching frequency is assigned to the peak at 957 cm^{-1}, this band was observed at 940 cm^{-1} in $K_2CrO_2(O_2CCF_3)_4$ (41). The spectrum indicates unidentate carboxylate linkage, in accord with the stoichiometry of the reaction.

A unique x-ray powder pattern was produced by the product with only the two strongest lines of K_2CrO_4 appearing as medium intensity lines.

Reaction of Sodium Molybdate and Sodium Tungstate with Perfluoroglutaric Anhydride. Reaction of perfluoroglutaric anhydride with the molybdenum and tungsten salts resulted in addition across only one of the metal-oxygen double bonds. It appears that the lower reactivity of these salts, relative to K_2CrO_4, is responsible for this fact, not simply an incomplete reaction, for further reaction with time was not noted after 1:1 stoichiometry was achieved.

The x-ray powder pattern for the tungsten compound (Table VII) is unique, with no lines for unreacted Na_2WO_4 present. While most of the diffraction pattern for the molybdenum compound was that of Na_2MoO_4 (therefore it is not reported), no unreacted Na_2MoO_4 appeared in the infrared spectrum. It is assumed that the molybdenum compound decomposed in the x-ray beam.

The infrared spectra of the tungstate and molybdate salts are listed in Table VI. The spectra are similar to the other perfluoroglutarate complexes except that the symmetric

CO_2 stretching modes are also split by about 20 cm^{-1}. The difference between the asymmetric and symmetric CO_2 stretching frequencies indicate that the carboxylate linkages to the metal in both compounds have considerable unidentate character. This persistence of unidentate carboxylate linkage, in all of the compounds discussed, may be the preferred configuration for coordination to metals when they are in high oxidation states.

The metal-oxygen stretching frequencies for these complexes are difficult to assign. It is tempting to identify the strong band at 945 cm^{-1} with M=O stretching, but the fact that the absorption appears at identical positions in both spectra makes this assignment somewhat suspect. In $WO_2(acac)_2$ the asymmetric and symmetric W=O stretching occurred at 954 and 968 cm^{-1}, but with $MoO_2(acac)_2$ only one band in the metal-oxygen double bond region (904 cm^{-1}) was found (53).

It appeared that the MoO_2^{+2} group was not bent, like the WO_2^{+2} group, therefore, this comparison may be a poor one for the molybdenum compounds. Molybdenum-oxygen double bonded stretching occurred at 961 cm^{-1} in the molybdenum(V) compound, $((acac)_2M{=}O)_2O$, (54). These examples show that Mo=O and W=O stretching occur in the same region and that small differences in band position could be masked by their broad nature. The Mo-O-C stretching band is assigned at 550 cm^{-1}. This band was observed at 576 and 550 cm^{-1} in $MoO_2(acac)_2$ (53).

CHAPTER IV

CHEMISTRY OF CHROMIUM OXIDE FLUORIDES

Introduction

Few properties of chromium oxide tetrafluoride, ($CrOF_4$), are known. They have been reviewed in Chapter I. It seems Edwards et al. (31) have been the only group able to prepare this compound. Their success is probably because of their fluorination apparatus, which was not described. The static system has a cooled zone which allows them to isolate the intermediate product ($CrOF_4$) in the stepwise elemental fluorination of CrO_3. Since the only reported chemistry of $CrOF_4$ is its fluorination to CrF_5, new preparative routes to $CrOF_4$ were sought with the intention to study its reaction chemistry. All new attempts to prepare $CrOF_4$ failed.

Various oxides and oxyfluorides were used as starting materials for the attempted preparations of $CrOF_4$. Chromyl fluoride was prepared by the methods of Green and Gard (27):

IV-1 $CrO_2Cl_2+2ClF\xrightarrow{-78^{\circ}C}CrO_2F_2+2Cl_2$

IV-2 $CrO_3+WF_6\xrightarrow{125^{\circ}C}CrO_2F_2+WOF_4$

The reactions were quantitative and are described in the experimental and discussion sections.

Chromium oxide difluoride was prepared from the thermal decomposition of chromyl fluoride (21):

IV-3 $CrO_2F_2\xrightarrow{550^{\circ}C}CrOF_2+\frac{1}{2}O_2$

The infrared spectrum of $CrOF_2$ is reported and an estimation was made of its surface area, as prepared.

Attempts to prepare $CrOF_4$ by a continuation of equations IV-2 and IV-5 failed.

IV-4 $CrO_2F_2+WF_6 \not\longrightarrow CrOF_4+WOF_4$

IV-5 $CrO_3+COF_2 \xrightarrow{185^\circ C} CrO_2F_2+CO_2$ (27)

IV-6 $CrO_2F_2+COF_2 \not\longrightarrow CrOF_4+CO_2$

Chromyl fluoride did not react with tungsten hexafluoride at temperatures up to its decomposition point (500°C). No reaction occurred between chromyl fluoride and carbonyl fluoride from 200°C to 350°C. At 400°C an incomplete reaction produced small amounts of O_2, CO_2, and CrF_3.

Direct fluorination of chromium oxide difluoride did not produce $CrOF_4$, but resulted in the loss of oxygen and oxidation to CrF_5:

IV-7 $CrOF_2+3/2F_2 \xrightarrow{250^\circ C} CrF_5+1/2O_2$

No reaction was observed between 25°C and 200°C.

Since new preparations for $CrOF_4$ were unsuccessful, the reported method of fluorination of CrO_3 at 220°C was tried. A top-loading Inconel vessel was equipped with a water-cooled jacket at the lid. It was found that the reaction products are not easily controlled by temperature:

IV-8 $CrO_3+5/2F_2(17\ atm) \xrightarrow{210^\circ C} CrF_5+3/2O_2$

IV-9 $CrO_3+F_2(2.6\ atm) \xrightarrow{190^\circ C} CrO_2F_2+\frac{1}{2}O_2$

The reactions were quantitative with no trace of $CrOF_4$ found. It appeared that the reaction products may be determined by the initial fluorine pressure as well, for even at 250°C it was reported that the products were a mixture of $CrOF_4$ and CrF_5 (31). Edwards prepared $CrOF_4$ with an initial fluorine pressure of 2 atmospheres. This fluorine pressure was used with CrO_2F_2 as the starting chromium species:

IV-10 $CrO_2F_2+F_2(2\ atm)\xrightarrow{200^\circ C}CrOF_4+\frac{1}{2}O_2(+CrO_2F_2)$

The reaction products were a mixture of CrO_2F_2 and $CrOF_4$.

Direct fluorination of CrO_3 was found to be difficult to control, with many attempts failing to produce $CrOF_4$. Chromium oxide tetrafluoride was not produced in sufficient quantities to study its physical properties or chemistry.

Experimental

Fluorination of Chromium Trioxide. A passivated 200 ml Inconel top-loading vessel containing 40 mmoles of CrO_3 was charged with 140 mmoles (17 atm) of F_2 at -196°C. The vessel lid was then equipped with a water-cooled cooling jacket and heated at 210°C. After 40 hours the excess F_2 was vented at room temperature, then the vessel was cooled to -78°C and was evacuated through a $CaCl_2$ tube. The $CaCl_2$ tube became hot, indicating unreacted fluorine:

IV-11 $F_2+CaCl_2\longrightarrow CaF_2+Cl_2+heat$

The vessel contents were non-volatile at room temperature. Upon opening the vessel, a deep red, stickey solid was found. The solid hydrolyzed violently to a yellow-green solution indicating a mixture of trivalent and hexavalent chromium. Most pentavalent chromium compounds disproportionate immediately in aqueous solution according to the equation:

IV-12 $3Cr^{V}\xrightarrow{H_2O}2Cr^{VI}+Cr^{III}$

The infrared spectrum of the product matched that of CrF_5 (55) with no extraneous absorbances present. The weight of the solids corresponded to 41 mmoles of CrF_5. The infrared spectrum appears in the appendix.

In a second run, 8 mmoles of CrO_3 was reacted with 21 mmoles (2.6 atm) of F_2 at 190°C. After 70 hours the vessel was cooled to -196°C and evacuated through a $CaCl_2$ tube. Again unreacted F_2 was indicated. The weight of the vessel contents corresponded to 8 mmoles of CrO_2F_2. At 20°C the vessel contents were volatile, and the infrared spectrum showed CrO_2F_2 to be the only compound present (36). Brief evacuation at room temperature resulted in the complete transfer of all material out of the vessel with no indication of the presence of $CrOF_4$.

Preparation of Chromyl Fluoride by the Reaction of Chromyl Chloride with Chlorine Monofluoride. Chlorine monofluoride, (100 mmoles), was condensed at -196°C into a passivated 75 ml stainless steel vessel containing 48 mmoles of CrO_2Cl_2. The vessel was warmed to -78°C and maintained at this temperature for 24 hours. Excess ClF and Cl_2 were pumped away at -78°C. The vessel was warmed to 20°C, shaken, then cooled to -78°C and evacuated for one hour. This proceedure was repeated three times to ensure the complete removal of ClF and Cl_2. The final weight of the vessel contents corresponded to 46 mmoles of CrO_2F_2. The infrared spectrum of chromyl fluoride appears in the appendix.

Preparation of Chromyl Fluoride by the Reaction of Chromium Trioxide with Tungsten Hexafluoride. Tungsten hexafluoride, (111 mmoles), was vacuum distilled into a passivated 75 ml stainless steel vessel containing 115 mmoles of CrO_3. The reaction mixture was heated at 120°C for 17 hours. Upon opening the vessel to the vacuum line at 20°C, the only volatile compound found was CrO_2F_2, as identified by its infrared spectrum (36). A total of 13.4 grams, (110 mmoles), of CrO_2F_2 was recovered.

Fluorination of Chromyl Fluoride. Freshly prepared CrO_2F_2, (19 mmoles), was sublimated into the 200 ml Inconel top loading vessel. The vessel was charged with 24 mmoles, (2 atm), of F_2 and heated at 200°C while cooling the lid. After 24 hours the vessel was evacuated at -196°C through a $CaCl_2$ tube, unreacted fluorine was indicated. The contents of the vessel were volatile at 20°C with CrO_2F_2 being the major component as identified by its characteristic infrared spectrum. One strong absorption was found at 1089 cm^{-1} which compares favorably with the calculated value of 1080 cm^{-1} for the chromium-oxygen stretching frequency of $CrOF_4$ (32). The vessel was evacuated briefly in an attempt to remove the CrO_2F_2, then the reactor was heated to 60°C while connected to a quartz vessel cooled to -196°C. A dark red solid transferred in vacuo to the quartz vessel very slowly, with the recovery of only .25 grams in 2 hours. The quartz vessel at 25°C contained a dark red solid that stuck to the stirring bar and a red to red-brown gas. The upper Pyrex-glass portions of the graded seal appeared to be coated with CrO_3. A low resolution infrared spectrum of the vessel atmosphere, which appears in the appendix, showed CrO_2F_2, SiF_4, again the strong absorption at 1089 cm^{-1} and an unidentified absorption at 1245 cm^{-1}. The dark red solids hydrolyzed to a yellow solution.

The reactor contained 1.8 grams of a non-volatile material. Upon opening the reactor in the dry box, a brown solid was found which also hydrolyzed to a yellow solution. An infrared spectrum of this solid revealed one strong absorption at 975 cm^{-1} due to chromium-oxygen stretching and a very strong, broad, complex chromium-fluorine stretching absorption which was unresolved from 850 cm^{-1} to 450 cm^{-1}. An attempted melting point determination of the solids in a Pyrex glass capillary resulted in glass attack at 45°C which became severe at 60°C.

<u>Reaction of Chromyl Fluoride with Carbonyl Fluoride</u>. To 33 mmoles of CrO_2F_2 contained in a 75 ml passivated stainless steel vessel was added 18 mmoles of COF_2 at -196°C via vacuum distillation. The reaction mixture was heated at 440°C for 4 hours, then cooled to -196°C. A non-condensible gas was present which was found by its molecular weight to be 13 mmoles of O_2. Requires: 32.0 grams/mole Found: 32.1 grams/mole. The infrared spectrum of the volatiles at 20°C showed CO_2, unreacted COF_2, and CrO_2F_2. After evacuation of the volatile materials, the vessel was found to contain 0.8 grams of an inert, light green solid which was identified as CrF_3, (7 mmoles), by its infrared spectrum (56). The spectrum appears in the appendix.

Reaction of Chromyl Fluoride with Tungsten Hexafluoride. Tungsten hexafluoride (17.4 mmoles) was vacuum distilled into a 75 ml passivated stainless steel vessel containing 11.5 mmoles of freshly prepared chromyl fluoride. The vessel was heated in a stepwise manner, for one day, at 110°C, 178°C, 252°C, 350°C, 440°C, and 550°C. An infrared spectrum of the volatiles at room temperature, made between each heating, revealed the presence of WF_6 and CrO_2F_2. After heating for one day at 550°C, the vessel was found to contain a non-condensable gas at -196°C. An infrared spectrum of the volatile contents at 20°C showed only WF_6. After the WF_6 was distilled away, the vessel was found to contain 2.6 grams of a mixture of gray, off white, and brown solids. The solids were insoluble in H_2O, an infrared spectrum qualitatively resembled the spectrum of $CrOF_2$ which appears in the appendix.

Preparation of Chromium Oxide Difluoride. Chromyl fluoride, (64 mmoles), was condensed into a 75 ml stainless steel vessel which had been passivated with fluorine at 400°C. The vessel was heated at 550°C for 5 hours, then chilled to -196°C. Upon opening the vessel to the vacuum manifold, a non-condensible gas was found which was identified as 31 mmoles of O_2, (32 mmoles theo.), by its molecular weight. Requires: 32.0 grams/mole Found: 32.06 grams/mole. Upon opening the vessel, a fine black powder was found which was insoluble in H_2O and anhydrous HF. The x-ray powder pattern of the product matches that of $CrOF_2$ (21) and is listed in Table IX. The weight of

$CrOF_2$ produced was 6.8 grams, (64 mmoles), for a yield of 100%. The infrared spectrum of the product is listed in Table X and appears in the appendix. This sample of chromium oxide difluoride was found to have a surface area of 0.59 square meters/gram.[2]

Fluorination of Chromium Oxide Difluoride. To a 100 ml passivated Monel vessel containing 9.4 mmoles of $CrOF_2$, was added 34 mmoles of F_2. The reaction mixture was slowly heated to 250°C over a period of 3 hours, then the vessel was cooled to -196°C and evacuated through a $CaCl_2$ tube. Excess fluorine was found to be present. An infrared spectrum of volatile materials at 20°C revealed only a trace of HF to be present. The vessel contained 1.3 grams of a dark red sticky semi-solid. The solids hydrolyzed violently to a yellow green solution and oxidized cotton explosively. An infrared spectrum of the solids matched that of CrF_5, (8.8 mmoles), which appears in the appendix.

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[2] The surface area measurement was made by Ms. Maria M. Ludvig at Portland State University. The author wishes to thank Ms. Ludvig for her assistance.

TABLE IX

EXPERIMENTAL AND LITERATURE (21) VALUES OF THE X-RAY POWDER PATTERN FOR $CrOF_2$

d (Å)	$CrOF_2$ Intensity	d (Å)	$CrOF_2$ (21) Intensity
6.38	s	6.32	s
5.89	m	5.84	s
4.17	w		
3.75	vs	3.75	s
3.64	w	3.66	m
3.53	w		
		3.24	vw
3.18	vs	3.17	vs
3.07	vw	3.06	w
		2.93	w
2.48	w	2.42	vw
		2.30	w
2.17	w	2.27	w
2.11	vw	2.11	vw
		2.07	vw
2.03	vw	2.01	vw
		1.98	vw
1.95	vw	1.95	w
1.88	w	1.88	w
1.83	w	1.83	m

TABLE X

INFRARED SPECTRUM OF $CrOF_2$ IN CM^{-1}

$CrOF_2$	Assignment
1010 m	ν (Cr=O)
1002 m	ν (Cr=O)
984 w	
920 m,b	ν (Cr-F or Cr-O-Cr)
730 m	ν (Cr-F)
565 vs,b	ν (Cr-F)
475 s	ν (Cr-F-Cr)
275 m	δ (F-Cr-F or O-Cr-F)

vs=very strong
s=strong
m=medium
w=weak
b=broad

Discussion

Fluorination of Chromium Trioxide and Chromium Dioxide Difluoride. Direct fluorination of CrO_3 at 20°C was exothermic, producing CrO_2F_2. In addition to temperature, the reaction products appear to be dependent on the fluorine pressure. Edwards et al. (31), with an initial fluorine pressure of 2 atmospheres, obtained CrO_2F_2 exclusively at 150°C. At 220°C a little CrO_2F_2 remained, but the major product was $CrOF_4$. Heating to 250°C produced mainly CrF_5 with a minor amount of $CrOF_4$. In contrast with these results, CrF_5 was found to be the only chromium species present when the initial fluorine pressure was 17 atmospheres, and a temperature of 210°C. Reducing the temperature to 190°C (but also reducing the initial fluorine pressure to 2.6 atmospheres) resulted in the quantitative conversion of CrO_3 to CrO_2F_2. This is a relatively small range of temperatures and fluorine pressures to work with in order to isolate $CrOF_4$. The problem may have been solved by a change in the reactor design. Close temperature control is needed as well as a cooled zone where the intermediate $CrOF_4$ can escape complete fluorination to CrF_5.

The fluorination of chromyl fluoride was carried out under the conditions reported by Edwards et al. The reactor containing CrO_2F_2 was charged with 2 atmospheres of F_2 and heated at 200°C. A mixture of CrO_2F_2 and $CrOF_4$ was obtained. Chromium oxide tetrafluoride was tentatively identified by its physical properties and by its previously reported attack of glass apparatus with the formation of CrO_2F_2 and CrO_3. Preliminary infrared spectral data for $CrOF_4$ in the gas phase indicates terminal chromium-oxygen stretching at 1089 cm^{-1}.

Fluorination of chromyl fluoride to $CrOF_4$, in the same region that Edwards et al. obtained $CrOF_4$ from CrO_3, seems to support his assumption that the reaction is a stepwise replacement of fluorine for oxygen.

Preparation of Chromyl Fluoride. Chromyl fluoride was prepared by two of the methods of Green and Gard (27), and were essentially quantitative. In the halogen exchange reaction between CrO_2Cl_2 and ClF, a slight excess of ClF must be used to ensure complete reaction and to prevent the formation of the mixed halide CrO_2ClF. Chromyl chlorofluoride can be distinguished from chromyl fluoride by a strong absorption band at 750 cm^{-1} (57). A large excess of ClF or temperatures above -78°C must be avoided however, or the yield of CrO_2F_2 decreases because of the formation of $CrOF_3 \cdot XClF$ (25).

The reaction of CrO_3 with WF_6 is the method of choice for the preparation of CrO_2F_2. The reactants are the least expensive and easiest to handle, when compared to the other methods reported thus far. Yields are quantitative at 120°C and as long as an excess of CrO_3 is maintained, pure CrO_2F_2 is easily recovered from CrO_3 and WOF_4 by vacuum sublimation at room temperature.

Reaction of Chromyl Fluoride with Carbonyl Fluoride and Tungsten Hexafluoride. Carbonyl fluoride and tungsten hexafluoride were found to be not powerful enough as fluorinating agents to produce $CrOF_4$ from CrO_2F_2. Carbonyl fluoride did not react with chromyl fluoride past 330°C. At 440°C some of the starting materials did react, by a seemingly complex mechanism, to produce O_2, CO_2, and CrF_3. A balanced equation is given below.

IV-13 $$2CrO_2F_2 + COF_2 \xrightarrow{440^\circ C} 2CrF_3 + 3/2O_2 + CO_2$$

Tungsten hexafluoride did not react past the decomposition point of chromyl fluoride. At 550°C chromium oxide difluoride was produced along with some attack of the vessel by WF_6.

Molybdenum hexafluoride was found to be more reactive than tungsten hexafluoride in the fluorination of CrO_3 to CrO_2F_2 (25). Possibly the fluorination reaction could be carried one step further to produce $CrOF_4$ with this reagent.

Preparation and Fluorination of Chromium Oxide Difluoride. Chromium oxide difluoride was prepared from the thermal decomposition of chromyl fluoride (21). The infrared spectrum of $CrOF_2$ is listed in Table X. The physical properties of $CrOF_2$ (non-volatility, insolubility in polar and non-polar solvents) indicate that it is extensively polymerized. Since the structure is unknown, direct normal mode assignments are not possible, but based on the group frequencies of other metal oxyfluorides, approximate assignments can be made. Terminal chromium-oxygen stretching is observed at 1010 cm^{-1} and 1002 cm^{-1}. The weak, unassigned absorption at 984 cm^{-1} is possibly a combination of chromium-fluorine stretching modes unresolved in the strong, broad band centered at 565 cm^{-1}. Absorption at 920 cm^{-1} is high for Cr-F stretching. The position and broad nature of the band suggest that it is more likely a bridged chromium-oxygen stretching mode. This vibration occurs at 893 cm^{-1} in CrO_3. Strong absorption bands between 840 cm^{-1} and 550 cm^{-1} are generally assigned to metal-fluorine stretching (58), although metal-fluorine bridged stretching modes may also occur at the lower end of this region. Bridged metal-fluorine stretching was assigned in the region of 440 cm^{-1} to 500 cm^{-1} in transition metal pentafluorides (59-61) and as high as 540 cm^{-1} in solid chromyl fluoride (62). The peak at 475 cm^{-1} is assigned as bridged chromium-fluorine stretching. This vibration was also assigned at 475 cm^{-1} in CrF_5 (55) and at 480 cm^{-1} in $CrOF_3$ (c. f. Chapter V). Absorption bands below 400 cm^{-1} are assigned to deformational modes.

The surface area of $CrOF_2$ was determined for future investigations into its possible catalytic activity. The value of 0.59 square meters/gram is somewhat disappointing for catalytic uses, but is within the range expected for crystalline solids.[3]

Fluorination of $CrOF_2$ at 250°C resulted in loss of oxygen and oxidation to CrF_5. No reaction was observed below 200°C and while $CrOF_4$ may be formed between 200°C and 250°C, no advantage can be seen in this possible preparation, over that of fluorination of CrO_3.

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[3] Personal communication, Dr. P. H. Emmett.

CHAPTER V

SYNTHESIS OF CHROMIUM OXIDE TRIFLUORIDE AND SOME REACTION CHEMISTRY

Introduction

Various halochromate(V) salts have been prepared but few have been isolated in pure form and well characterized (63, 64). The only known neutral chromium(V) compounds are chromium pentafluoride, (CrF_5), chromium oxide trichloride, ($CrOCl_3$), and chromium oxide trifluoride, ($CrOF_3$), which until now has never been obtained in pure form.

Hexavalent chromium compounds are usually reduced to the pentavalent state upon strong halogenation. Chromium oxide trichloride was first prepared by Krauss et al, as a minor by-product in the reaction of chromium trioxide with either thionyl chloride or sulfuryl chloride (65, 66):

V-1 $CrO_3+SOCl_2 \xrightarrow{0^\circ C} CrO_2Cl_2+SO_2$

$CrO_2Cl_2+SOCl_2 \longrightarrow CrOCl_3+SO_2+\frac{1}{2}Cl_2$

V-2 $CrO_3+SO_2Cl_2 \xrightarrow{0^\circ C} CrO_2Cl_2+SO_3$

$CrO_2Cl_2+SO_2Cl_2 \longrightarrow CrOCl_3+SO_3+\frac{1}{2}Cl_2$

The major product of the reactions is chromyl chloride, but the less volatile $CrOCl_3$ can be isolated in two percent yield by fractional distillation of the reaction mixture. Higher yields of $CrOCl_3$ are obtained by the reaction of CrO_2Cl_2 with BCl_3 (67):

V-3 $CrO_2Cl_2+2/3BCl_3 \longrightarrow \underset{50\%\ \text{yield}}{CrOCl_3}+1/3B_2O_3+\frac{1}{2}Cl_2$

Chromium oxide trichloride is unstable at room temperature, disproportionating to CrO_2Cl_2 and presumably $CrCl_3$.

A recent investigation of the spectral properties of $CrOCl_3$ (68), indicates that by analogy to $VOCl_3$, the vapor phase species is mono-molecular with a trigonal pyramidal structure (C_{3v} symmetry), but in the solid state a chlorine-bridged polymer is indicated.

Chromium pentafluoride can be prepared by direct fluorination of chromium metal (69), CrF_3 (70), or CrO_3 (31). The initial product is believed to be CrF_6 which is unstable above -100°C, decomposing to CrF_5 and F_2 (71).

Chromium trioxide has been found to react with the strong fluorinating agents BrF_3, BrF_5, and ClF_3, to produce $CrOF_3\cdot.25BrF_3$, $CrOF_3\cdot.25BrF_5$, and $CrOF_3\cdot.30ClF_3$ (24). Again, chromium has been reduced to the pentavalent state, but only partial fluorination has occurred. Attempts to remove the particular interhalogen fluorinating agent by heating the products in vacuo resulted in decomposition, although reaction of $K_2Cr_2O_7$ with BrF_3 produced $KCrOF_4\cdot.5BrF_3$ which when heated in vacuo at 160°C, yielded pure $KCrOF_4$ (24).

In the preparation of chromyl fluoride from CrO_3 and ClF, Green (25) noted that a large excess of ClF or a reaction temperature above 0°C, caused a reduction in the yield of CrO_2F_2 and formation of an unstable brick red solid. This solid hydrolyzed to a yellow-green solution and had a magnetic moment consistent with a d^1 chromium(V) compound. As with the previous work with interhalogen fluorides, elemental analysis indicated an impure product of composition $CrOF_3\cdot .14ClF$ to $CrOF_3\cdot .21ClF$.

In an attempt to prepare $CrOF_4$, the $CrOF_3\cdot XClF$ was reacted with fluorine at 120°C. The product of this reaction was a non-volatile purple solid with a greatly reduced chlorine content. Elemental analysis of the purple product gave an approximate composition of $CrOF_3$.

In an extension of this work, the reaction of CrO_3 and ClF at 110°C was found to yield unstable adducts of $CrOF_3$ (and apparently ClF) of non-stoichometric composition:

V-3 $CrO_3+(4\text{ to }5)ClF\xrightarrow{100^{\circ}C}CrOF_3\cdot xClF+O_2+3/2Cl_2+yClO_2F$

The equation is unbalanced because ClF appears to be incorporated in some form with the product, and is also consumed by the formation of ClO_2F.

The chlorine containing $CrOF_3$ was heated at 120°C in a fluorine atmosphere.

V-4 $CrOF_3\cdot xClF+F_2\xrightarrow[4\text{ hours}]{1\text{ atm.}}CrOF_3+F_2+ClO_2F$

Multiple fluorine treatments yields a bright purple solid which was shown by elemental analysis to be essentially free from chlorine. The only volatile product of the fluorine treatments giving an infrared spectrum was ClO_2F (72). Infrared spectral data suggests that $CrOF_3$ is a fluorine-bridged polymer with terminal oxygen groups. An x-ray powder pattern was also measured.

Pure $CrOF_3$ was found to be stable to 300°C where it appears to melt with decomposition, producing oxygen and CrF_3.

V-5 $CrOF_3 \xrightarrow{500^\circ C} \frac{1}{2}O_2 + CrF_3$

Chromium oxide trifluoride was found to react with fluorine at elevated temperatures with the loss of oxygen to produce CrF_5.

V-6 $CrOF_3 + F_2 \xrightarrow{190^\circ C} CrF_5 + \frac{1}{2}O_2$

A limited study of the reaction chemistry of pure $CrOF_3$ was undertaken. With the Lewis bases, KF and NO_2F; 1:1 adducts were formed:

V-7 $CrOF_3 + KF \xrightarrow{HF} KCrOF_4$

V-8 $CrOF_3 + NO_2F \longrightarrow NO_2CrOF_4$

Infrared spectral data indicates that a monomeric, square pyramidal $CrOF_4^-$ anion, (C_{4v} symmetry), is present in both of these compounds and that the nitryl salt contains a linear ONO^+ cation. X-ray powder patterns were also measured.

Reaction of $CrOF_3$ with the strong Lewis acid, SbF_5, resulted in the loss of oxygen and formation of a 1:2 adduct.

V-9 $CrOF_3 + 2SbF_5 \longrightarrow CrF_2Sb_2F_{11} + \frac{1}{2}O_2$

The ultraviolet spectrum of the product in DMSO is consistent with a chromium (III) compound and infrared data indicates the presence of the $Sb_2F_{11}^-$ anion.

Chromium oxide trifluoride was found to be insoluble and unreactive with WF_6 at 110°C.

Experimental

Preparation of Chromium Oxide Trifluoride. Dried CrO_3, (35 mmoles), was added to a passivated 100 ml Monel vessel in the dry box. Chlorine monofluoride, (151 mmoles), was then condensed into the vessel at -196°C and the reaction mixture was heated at 110°C for 4 hours with periodic shaking. Upon opening the vessel at -196°C, a gas was found which was identified as oxygen by its molecular weight. Requires: 32.0 grams/mole Found: 31.7 grams/mole. At -78°C, the volatile materials consisted of ClF and ClO_2F, identified by their infrared spectra (34, 72) and Cl_2, a yellow-green liquid at -78°C. No volatile materials were found at 20°C, the weight of the vessel contents corresponded to $CrOF_3 \cdot 0.1ClF$.

The vessel containing the chlorine contaminated $CrOF_3$ was charged with 1.2 atm. of fluorine and heated at 120°C for 12 hours. After cooling to -196°C, the vessel was evacuated through a $CaCl_2$ tube, fluorine was indicated. At 20°C the vessel contained 850 mm of volatiles, identified as ClO_2F by its infrared spectrum. The vessel was evacuated and again charged with 1.2 atm. of fluorine, then heated at 120°C for 2 hours. After removal of the fluorine, 60 mm of volatiles were found at 20°C, ClO_2F was the only infrared active material present. The vessel contents were treated with 1.2 atm. of fluorine a third time at 120°C for 3 hours, only 5 mm of volatiles were found at 20°C.

After evacuation, the vessel was opened in the dry box and found to contain 4.3 grams, (34 mmoles), of $CrOF_3$, a non-volatile, bright purple solid. Analysis for $CrOF_3$-Cr; Requires: 41.6% Found: 41.72%, F; Requires: 45.6% Found: 45.4%, Cl; Found: 0.49%. Purple $CrOF_3$ is mildly hygroscopic, turning dark in air, and hydrolyzes to a yellow-green solution. The compound slowly attacks glass above 230°C, but at 300°C there is sudden, extensive glass attack with apparent melting. Chromium oxide trifluoride attacks acetone, hexane, DMSO, and is insoluble in CCl_4. Preliminary work suggests that $CrOF_3$ is slightly soluble in anhydrous HF and BrF_3. The x-ray powder pattern is listed in Table XI. An infrared spectrum is given in Table XII, and also appears in the appendix.

Thermal Decomposition of Chromium Oxide Trifluoride. To a well-passivated 100 ml Monel vessel was added 33 mmoles of $CrOF_3$. The vessel was placed in a tube furnace and heated to 500°C over a period of 5 hours, then cooled to -196°C. Upon opening the vessel to the vacuum manifold, a non-condensable gas was found which was identified as oxygen, (16 mmoles), by its molecular weight. Requires: 32.0 grams/mole Found: 32.2 grams/mole. At 20°C no other volatile materials were present. The vessel contained an inert, light green solid which was identified as CrF_3, (34 mmoles), by its infrared spectrum and x-ray powder pattern which is listed in Table XIII. Analysis for CrF_3-Cr; Requires: 47.7% Found: 44.72%, F; Requires: 52.3% Found: 48.4%.

Fluorination of Chromium Oxide Trifluoride. Fluorine, (71 mmoles), was condensed at -196°C into a passivated 100 ml Monel vessel containing 40 mmoles of $CrOF_3$. The reaction mixture was heated at 190°C for 15 hours, then the excess fluorine was removed at -196°C. At 20°C no volatile materials were present. The vessel was found to be coated with

TABLE XI

X-RAY POWDER PATTERN OF CrOF$_3$

d (Å)	Intensity	d (Å)	Intensity
4.96	m	1.95	w
4.46	s	1.89	w
4.04	m	1.86	vw
3.76	s	1.82	m
3.64	s	1.69	m
3.37	vs	1.58	s
2.83	w	1.53	w
2.75	vw	1.49	w
2.58	m	1.46	vw
2.48	s	1.43	m
2.24	s	1.41	m
2.04	m	1.20	m
2.01	w		

vs=very strong
s=strong
m=medium
w=weak
vw=very weak

TABLE XII

VIBRATIONAL FREQUENCIES OF SOLID $CrOF_3$, VOF_3 (60), AND $MoOF_3$ (73) IN CM^{-1}

$CrOF_3$			VOF_3	$MoOF_3$
IR	Raman*	Assignment	Raman	IR
1000 s	1000 s	$\nu(\text{Cr=O})$	1039 vs	1000 s
785 w	789 w	512 + 270		
718 s	714 m,b; w/shoulder at 740	$\nu(\text{Cr-F})$	741 s	
682 s	690 m	$\nu(\text{Cr-F})$	678 w	680
600 vs	607 w	$\nu(\text{Cr-F})$	620 m	625
565 s	562 vw?	$\nu(\text{Cr-F})$	530 m	545
512 s	527 m	$\nu(\text{Cr-F-Cr?})$**		
480 m	473 m	$\nu(\text{Cr-F-Cr?})$**		490
	450 m	$\delta(\text{F-Cr-F})$ and $\delta(\text{O=Cr-F})$		
380 w	395 s		408 vw	
350 vw	354 s; w/shoulder at 337		358 m	
330 w			326 s	
	291 s			
270 m	269 ms		312 vw	
			232 s	
	190 vs		216 m	
			172 vw	
			138 m	

*Spectrum obtained from Dr. Tom M. Loehr at the Oregon Graduate Center.

**Two types of fluorine bridging were found in solid VOF_3 (80), but one of these bands may be due to chromium-fluorine stretching or bending.

TABLE XIII

X-RAY POWDER PATTERNS OF THE $CrOF_3$ DECOMPOSITION PRODUCT AND CrF_3 (74)

$CrOF_3 \xrightarrow{500^\circ C} CrF_3$		CrF_3
d (Å)	Intensity	d (Å)
4.00	m	
3.62	vs	3.60_{100}
2.90	vw	
2.62	w	2.61_{20}
2.50	vw	2.48_{8}
2.40	vw	
2.17	m	2.17_{30}
2.00	w	2.05_{6}
1.81	m	1.80_{20}
1.64	ms	1.65_{30}
1.58	w	1.58_{16}
1.53	vw	
1.46	vw	1.46_{10}
1.44	vw	1.44_{16}

vs=very strong
m=medium
w=weak
vw=very weak

a deep red semisolid which fumed in air, hydrolyzed to a yellow-green solution, and ignited acetone. An infrared spectrum of the solid showed it to be CrF_5, (35 mmoles), produced in 88% yield.

Reaction of Chromium Oxide Trifluoride with Potassium Fluoride. Chromium oxide trifluoride, (26 mmoles), and potassium fluoride, (26 mmoles) were placed in a 40 ml Kel-F vessel in the dry box. Anhydrous hydrogen fluoride, (0.71 moles), was vacuum distilled into the vessel and the mixture was magnetically stirred for 1 hour. A deep purple solution formed immediately and no solids could be detected in the translucent vessel. After evacuation of the vessel at 40°C, a weight pickup of 25 mmoles HF, ($KCrOF_4 \cdot HF$), was found. Evacuation of the vessel at 100°C for 1 hour removed all of the residual HF, leaving behind solids which equaled the original weight of the reactants.

The vessel contents were a tan-green crystalline solid which darkened in moist air and hydrolyzed to a yellow-green solution. Analysis for $KCrOF_4$-Cr; Requires: 28.4% Found: 28.26%, F; Requires: 41.5% Found: 42.5%. The product did not melt at temperatures above 400 C but attacked the glass capillary above 170°C. An x-ray powder pattern was obtained which correlated well with a pattern calculated from the unit cell constant data of Clark and Sadana (24) for $KCrOF_4$.[4]

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[4] The x-ray powder pattern was calculated with the help of a computer program (75) adapted with modifications for the Honeywell H-66/20 by Dr. Bruce W. Brown of Portland State University. The author wishes to thank Dr. Brown for his assistance.

The x-ray pattern showed no unreacted KF or $CrOF_3$ and is listed in Table XIV. The infrared spectrum of the product is listed in Table XV and also appears in the appendix.

Reaction of Chromium Oxide Trifluoride with Nitryl Fluoride. Purified NO_2F, (77 mmoles), was condensed at -196°C into a passivated 75 ml stainless steel vessel containing 21 mmoles $CrOF_3$. The vessel was heated at 50°C for 11 days with periodic shaking. Upon evacuation of the vessel, no non-condensables were found at -196°C. At 20°C the only volatile substance was NO_2F, identified by its infrared spectrum (38). The weight pickup of the vessel corresponded to 21 mmoles of NO_2F. The vessel contents were a non-volatile tan colored powder which was mildly hygroscopic, hydrolyzing to a yellow-green solution. Analysis for NO_2CrOF_4-N; Requires: 7.4% Found: 5.91%, Cr; Requires: 27.4% Found: 29.49%, F; Requires: 40.0% Found: 41.9%. The product decomposes above 80°C evolving a brown gas, probably NO_2. A unique x-ray powder pattern was obtained which is listed in Table XVI. The x-ray pattern shows that no unreacted $CrOF_3$ is present. The infrared spectra of the product differ when the sample is prepared as a KBr pellet, compared to a Nujol mull between KRS-5 plates. The spectra are listed in Table XVII, and the Nujol mull spectrum appears in the appendix.

Reaction of Chromium Oxide Trifluoride with Antimony Pentafluoride. To a 68 ml quartz vessel was added 2.75 mmoles of $CrOF_3$ and 59 mmoles of SbF_5 via vacuum distillation. The reaction mixture was heated at 110°C for 13 days

TABLE XIV

OBSERVED AND CALCULATED (24) X-RAY POWDER PATTERNS FOR $KCrOF_4$

Observed		Calculated	Observed		Calculated
d (Å)	Intensity	d (Å)	d (Å)	Intensity	d (Å)
8.12	m	8.13	2.64	w	2.64
5.56	s	5.57	2.58	w	2.58
5.17	s	5.18	2.38	w	2.38
4.90	m	4.80	2.35	w	2.35
4.70	m	4.63	2.33	w	2.31
4.37	m	4.38	2.30	w	2.99
4.21	s	4.16	2.21	m	2.18
4.06	w	4.06	2.16	m	2.16
3.97	w	3.97	2.02	vw	2.02
3.51	w	3.52	1.99	vw	1.98
3.46	w	3.44	1.97	vw	1.97
3.35	s	3.35	1.95	vw	1.95
3.29	s	3.31	1.94	vw	1.94
3.23	s	3.24	1.91	m	1.91
2.70	w	2.70	1.87	w	1.87

s=strong
m=medium
w=weak
vw=very weak

TABLE XV

INFRARED SPECTRA OF $KCrOF_4$ AND $CsVOF_4$ (76) IN CM^{-1}

$KCrOF_4$	Assignment	$CsVOF_4$
1020 s	ν (Cr=O)	1023 vs
		1016 vs
962 w	$\frac{640+350}{625+335}$	973 w
	1023-310	713 w
640 vs,b	ν (Cr-F)	625 s
500 s	ν (Cr-F)	595 s
		480 m
350 m	δ (F-Cr-F) and	335 s
285 m	δ (O=Cr-F)	310 m
	595-335	260 m

vs=very strong
s=strong
m=medium
w=weak
b=broad

TABLE XVI

X-RAY POWDER PATTERN OF NO_2CrOF_4

d (Å)	Intensity	d (Å)	Intensity
5.45	m	2.47	w
5.21	m	2.24	w
4.91	s	2.18	w
4.48	m	1.82	w
4.04	s	1.78	w
3.73	w	1.69	w
3.37	s	1.60	w
3.06	w		

s=strong
m=medium
w=weak

vs=very strong
vb=very broad

TABLE XVII

INFRARED SPECTRA OF NO_2CrOF_4 IN CM^{-1}

KBr Pellet	Assignment	Nujol Mull
2280 m	ν (asym NO_2^+)	2285 s
2070 w		
1815 s		
1500 s		
1380 w	ν (sym NO_2^+)	
1300 m		
1255 w		
985 s	ν (Cr=O)	980 s
	ν (Cr-F)	700 s
530 vs,vb	ν (Cr-F)	540 vs,vb

resulting in a red-brown solution. After evacuation of the vessel for 5 hours at 40°C, a red-brown solid was obtained. The weight pickup of the vessel corresponded to 13.8 mmoles of SbF_5 or an apparent stoichiometry of $CrF_3 \cdot 5.0SbF_5$, subjecting the red-brown solid to a dynamic vacuum while heating at 100°C for 35 hours, produced a light green powder. The non-volatile product at constant weight corresponded to $CrF_3 \cdot 2SbF_5$. Analysis for $CrF_2Sb_2F_{11}$-Cr; Requires: 10.4% Found: 11.21%, F; Requires: 45.5% Found: 44.7%. The product is very hygroscopic, hydrolyzing violently to a green solution. Heating the green powder in a glass capillary resulted in no melting past 400°C, but glass attack was apparent above 200°C. The ultraviolet spectrum of the product in DMSO showed two absorption bands with the start of a third; 450 nm (ϵ =49 liter mole^{-1} cm^{-1}) and 652 nm (ϵ =30 liter mole^{-1} cm^{-1}). X-ray analysis resulted in no diffraction, indicating that the compound is amorphous. The infrared spectrum is listed in Table XVIII and also appears in the appendix.

Interaction of Chromium Oxide Trifluoride and Tungsten Hexafluoride. Chromium oxide trifluoride, (7.2 mmoles), was added to a 75 ml passivated stainless steel vessel. Tungsten hexafluoride, (47 mmoles), was vacuum distilled into the vessel and the mixture was heated at 110°C for 3 days. The vessel was evacuated at 30°C through a -196°C-cooled trap. No non-condensables were found, all but 1 mmole of the WF_6 was recovered. The vessel contained a bright purple powder which was confirmed to be $CrOF_3$ by its infrared spectrum.

TABLE XVIII

INFRARED SPECTRA OF $CrF_2Sb_2F_{11}$ AND $CrF_4Sb_2F_{11}$ (77) IN CM^{-1}

$CrF_2Sb_2F_{11}$	Assignment	$CrF_4Sb_2F_{11}$
865 m	ν (Cr-F?)	830 s
	ν (Cr-F)	780 m
680 s	ν (Sb-F)	695 s
660 vs	ν (Sb-F)	665 s
545 s,b	ν (Sb-F-Sb)	525 s,b
280 w	δ (Cr-F)	280 w

vs=very strong
s=strong
m=medium
b=broad

Discussion

Preparation and Purification of Chromium Oxide Trifluoride. Reaction of CrO_3 with ClF at 110°C produced a brick red, unstable solid. As was found in the reaction of CrO_3 with other interhalogen fluorides (22, 24), the product appeared to be an adduct of $CrOF_3$ and the interhalogen fluorinating agent.

It is interesting that when the impure $CrOF_3$ is purified by heating at 120°C in a fluorine atmosphere, ClO_2F, not ClF, is the only by-product yielding an infrared spectrum. It appears that the contaminating species may be $ClO_2^+CrOF_4^-$. This speculation is supported by infrared spectral data of the impure $CrOF_3$. Weak absorption bands are found at 1275 cm^{-1} and 1062 cm^{-1}. Asymmetric and symmetric ClO_2^+ stretching is observed at 1296 cm^{-1} and 1044 cm^{-1} in $ClO_2^+AsF_6^-$, and at 1294 cm^{-1} and between 1100 cm^{-1} and 990 cm^{-1} in $ClO_2^+BF_4^-$ (78).

The purification of $CrOF_3$ with fluorine is limited to temperatures between 120°C and 190°C. Below 120°C the interactions ineffective and removal of the contaminating species is incomplete. At temperatures near 190°C, $CrOF_3$ is fluorinated to CrF_5.

The infrared spectrum of $CrOF_3$, listed in Table XII, is of high quality and reproducible when displayed as a neat solid between KRS-5 plates or as a KBr pellet. The physical properties of $CrOF_3$ (non-volatility, insolubility in non-polar solvents) indicate that it is polymerized in the solid state, this makes definite spectral assignments and comparisons to compounds of known structure difficult. The polymeric nature of solid $CrOF_3$ is confirmed by the multiplicity of absorption bands in the chromium-fluorine stretching region between 718 cm^{-1} and 565 cm^{-1}, and by the absorptions at 512 cm^{-1} and 480 cm^{-1} which are in the region of chromium-fluorine bridge bonded stretching (59-61). In the Raman spectra, fluorine-bridged bond stretching bands are usually weak (60, 79); however, with solid CrO_2F_2 and in solid $CrOF_3$ they are present as medium intensity bands (62). Terminal chromium-oxygen stretching is clearly indicated by the absorption bands at 1000 cm^{-1}, both in the infrared, and in the Raman spectrum of $CrOF_3$. No bands are attributable to chromium-oxygen bridging (52).

An unassigned infrared spectrum of $MoOF_3$ has appeared in the Russian literature (73), but the spectrum of $CrOF_3$ correlates more closely with VOF_3 which suggests that they may be isostructural. The solid state structure of VOF_3 has been determined (80) and is illustrated in Figure 10.

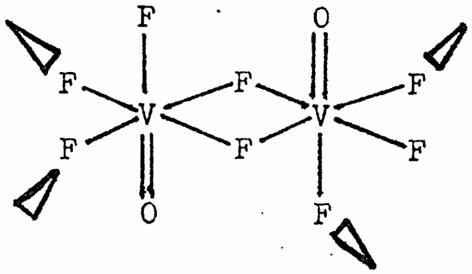
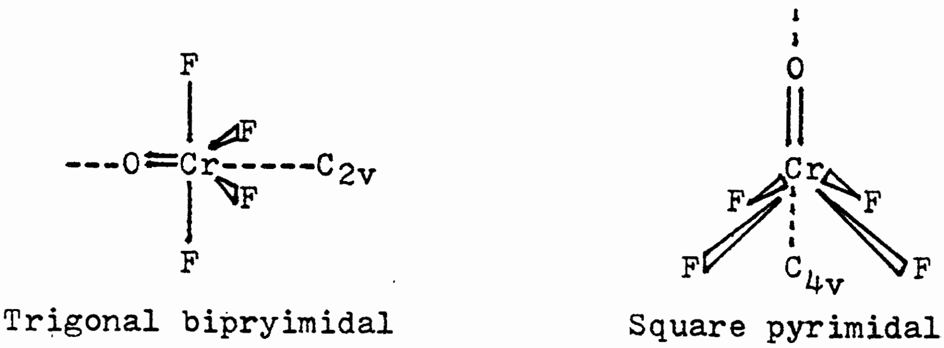


Figure 10. Structure of solid VOF_3.

Chromium oxide trifluoride appears to melt with decomposition at 300°C when heated in a glass capillary. When a sample of $CrOF_3$ was sealed in a well passivated Monel vessel and heated at 500°C, quantitative decomposition to CrF_3 and oxygen was observed. This decomposition behavior is similar to that of chromyl fluoride, which loses oxygen at 500°C (21).

Reaction of Potassium Fluoride with Chromium Oxide Trifluoride. In anhydrous HF, the reaction of KF and $CrOF_3$ not only produced $KCrOF_4$, but apparently a 1:1 adduct was formed with the solvent. The $HF \cdot KCrOF_4$ adduct presumably could contain the bifluoride cation KHF^+. This adduct was not further studied. The coordinated HF was removed by heating the adduct at 100°C in vacuo.

The infrared spectrum of $KCrOF_4$ is listed in Table XIV. No absorption bands appear in the regions assigned to chromium-oxygen or chromium-fluorine bridging. The absence of these bands indicate a square pyramidal (C_{4v} symmetry) or a trigonal bipyrimidal (C_{2v} symmetry) structure for the monomeric $CrOF_4^-$ anion. These two possible structures are illustrated in Figure 11.



Trigonal bipryimidal

Square pyrimidal

Figure 11. Possible structures of the $CrOF_4^-$ anion.

The total number of vibrations allowed for the $CrOF_4^-$ anion is 12. In C_{2v} symmetry the expected number of infrared active vibrational frequencies is 11 and for C_{4v} symmetry there are 6 expected infrared active bands. The infrared spectrum of $KCrOF_4$ strongly suggests C_{4v} symmetry (by comparison with the vibrational spectrum of $CsVOF_4$ (81), for which C_{4v} symmetry is assumed). The only anomalies in the spectra are the split V=O stretch which was explained by the authors as a solid state effect (81), and the absence of a sixth absorption band in $KCrOF_4$, which is probably unresolved in the strong, broad absorptions around 600 cm^{-1}

Assignment of C_{4v} symmetry to the $CrOF_4^-$ anion is not surprising, this structure has been assumed for many oxo-tetrachloro chromate(V) salts (64) and has been confirmed for $(AsPh_4)(CrOCl_4)$ in an x-ray crystallographic study (82).

Reaction of Nitryl Fluoride with Chromium Oxide Trifluoride. Direct reaction of solid $CrOF_3$ with gaseous NO_2F produced NO_2CrOF_4. The tan solid is non-volatile and decomposes above 80°C, giving off a brown gas. Similar decomposition behavior was found for $NO_2CrO_2F_3$ (29) and NO_2CrF_6 (77), which decompose at 130°C and 142°C.

The infrared spectrum of NO_2CrOF_4 closely resembles $KCrOF_4$ in the low frequency region. This indicates a square pyramidal structure for the anion in NO_2CrOF_4. The high frequency region of the spectrum is confusing when the sample is displayed as a KBr pellet. A multitude of bands appear which cannot be accounted for by a simple NO_2^+ cation. When the sample is displayed as a Nujol mull between KRS-5 plates, all but one of the high frequency bands disappear. Reaction of nitryl salts with sodium chloride and barium fluoride windows has been observed (83, 84), requiring the use of the more inert silver chloride plates for obtaining infrared spectra.

A total of three vibrations are expected for the nitronium cation. If the NO_2^+ group is bent, all three vibrations would be infrared active. For a linear ONO^+ ion, only the asymmetric stretching and bending vibrations would be infrared active (85). The Nujol mull spectrum of NO_2CrOF_4, listed in Table XVII, supports a linear structure for the ONO^+ cation. Asymmetric stretching is observed at 2285 cm^{-1}, this band was found at 2315 cm^{-1} in NO_2CrF_6 (77). The symmetric NO_2^+ stretch is missing, as expected. This band should occur around 1400 cm^{-1} (86), and may be represented at 1380 cm^{-1} in the KBr pellet spectrum as the result of distortion of the linear ONO^+ symmetry by pellet interactions. The bending mode should be observed in the infrared, but this band is expected around 650 cm^{-1} (86) and is therefore masked by the strong, broad chromium-fluorine stretching modes.

Reaction of Chromium Oxide Trifluoride with Antimony Pentafluoride. Attempts were made to prepare an adduct of $CrOF_3$ with SbF_5. However, the reaction proceeded with reduction of $CrOF_3$ by the loss of oxygen. After removal of the excess SbF_5, an initial solid product was obtained which had an apparent stiochiometry of $CrF_3 \cdot 5.0SbF_5$. This solid was not studied, further evacuation at 100°C resulted in a constant weight adduct of composition $CrF_3 \cdot 2SbF_5$.

An ultraviolet spectrum of the 1:2 adduct in DMSO gave two absorption bands at 450 nm (ϵ =49 liter mole^{-1} cm^{-1}) and 652 nm (ϵ =30 liter mole^{-1} cm^{-1}). These values correlate well with the spectrum of $(Cr(DMSO)_6)(ClO_4)_3$ (87), which absorbs at 444 nm (ϵ =33.4 liter mole^{-1} cm^{-1}) and 634 nm (ϵ =34.6 liter mole^{-1} cm^{-1}).

The light green product did not give an x-ray powder pattern and would indicate that it is amorphous, but this may also be the result of poor crystal growth during its formation.

The infrared spectrum of $CrF_3 \cdot 2SbF_5$ is listed in Table XVIII. Comparison with the spectrum of $CrF_4Sb_2F_{11}$ (77) indicates that the adduct contains the $Sb_2F_{11}^-$ anion and is therefore formulated as $CrF_2Sb_2F_{11}$. The medium absorption band at 865 cm^{-1} occurs at a high frequency to be safely assigned as chromium-fluorine stretching, although a chromium-fluorine stretching mode also occurred at significantly higher frequency in $CrF_4Sb_2F_{11}$ than in CrF_5 (77).

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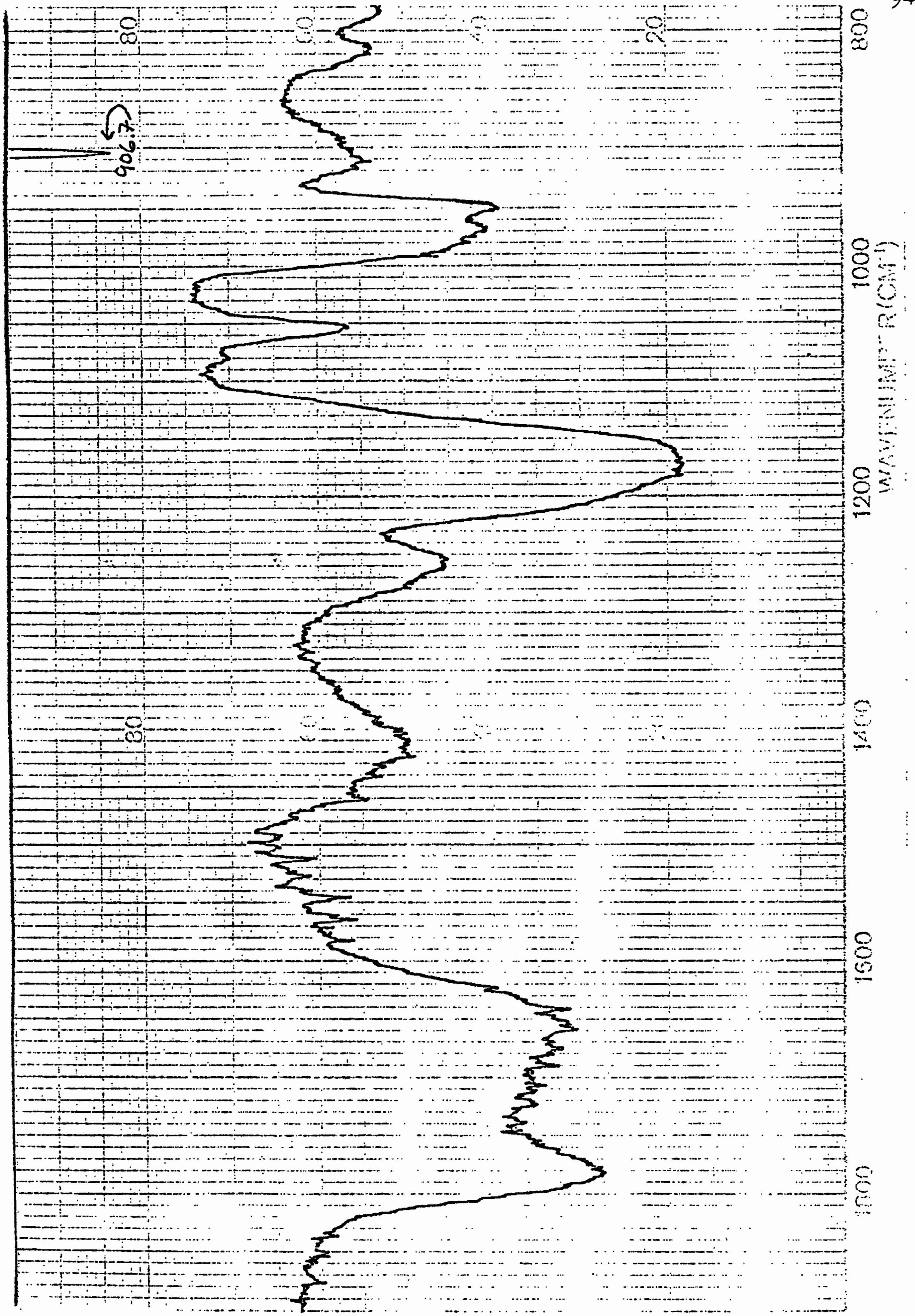
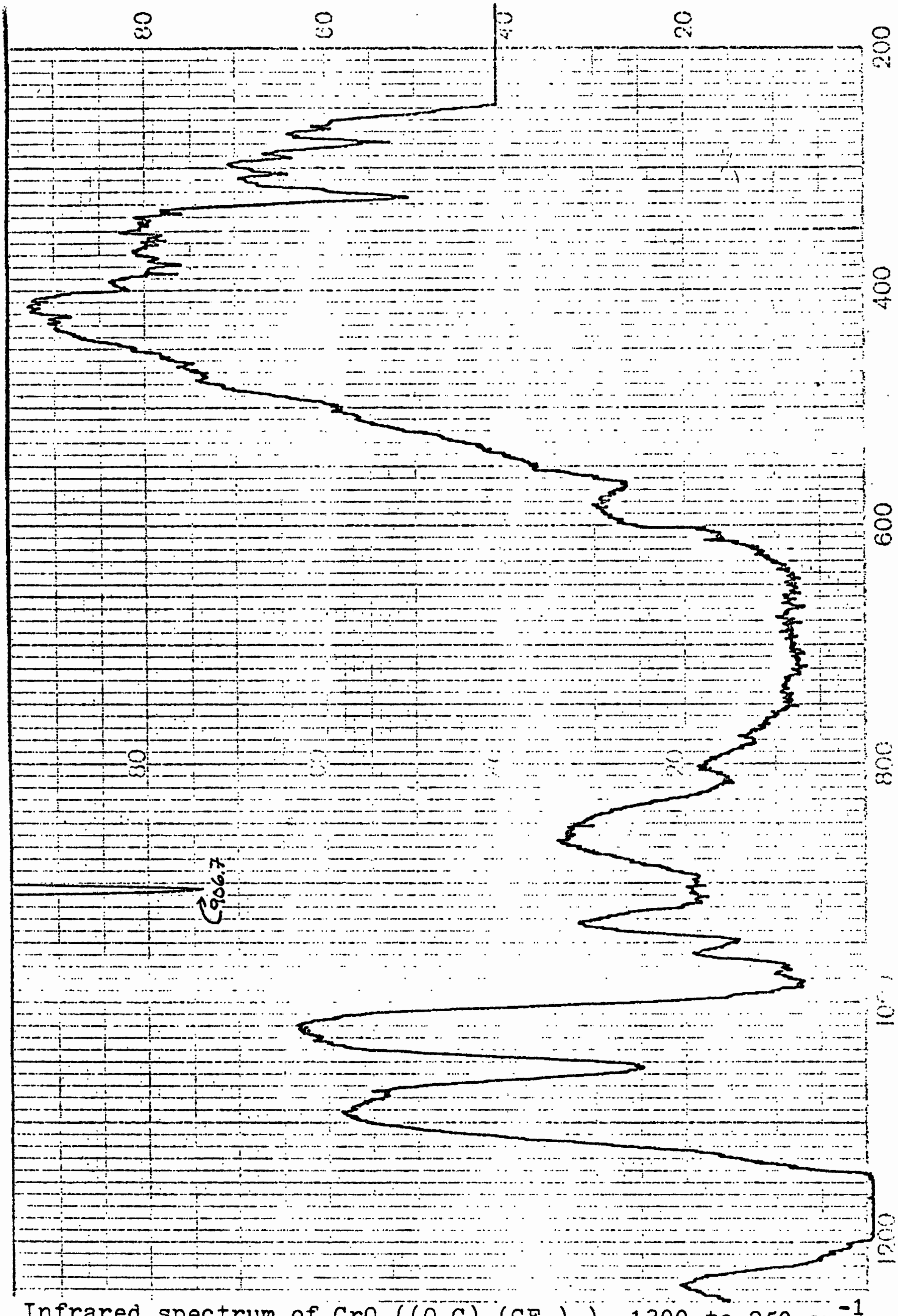
APPENDIX

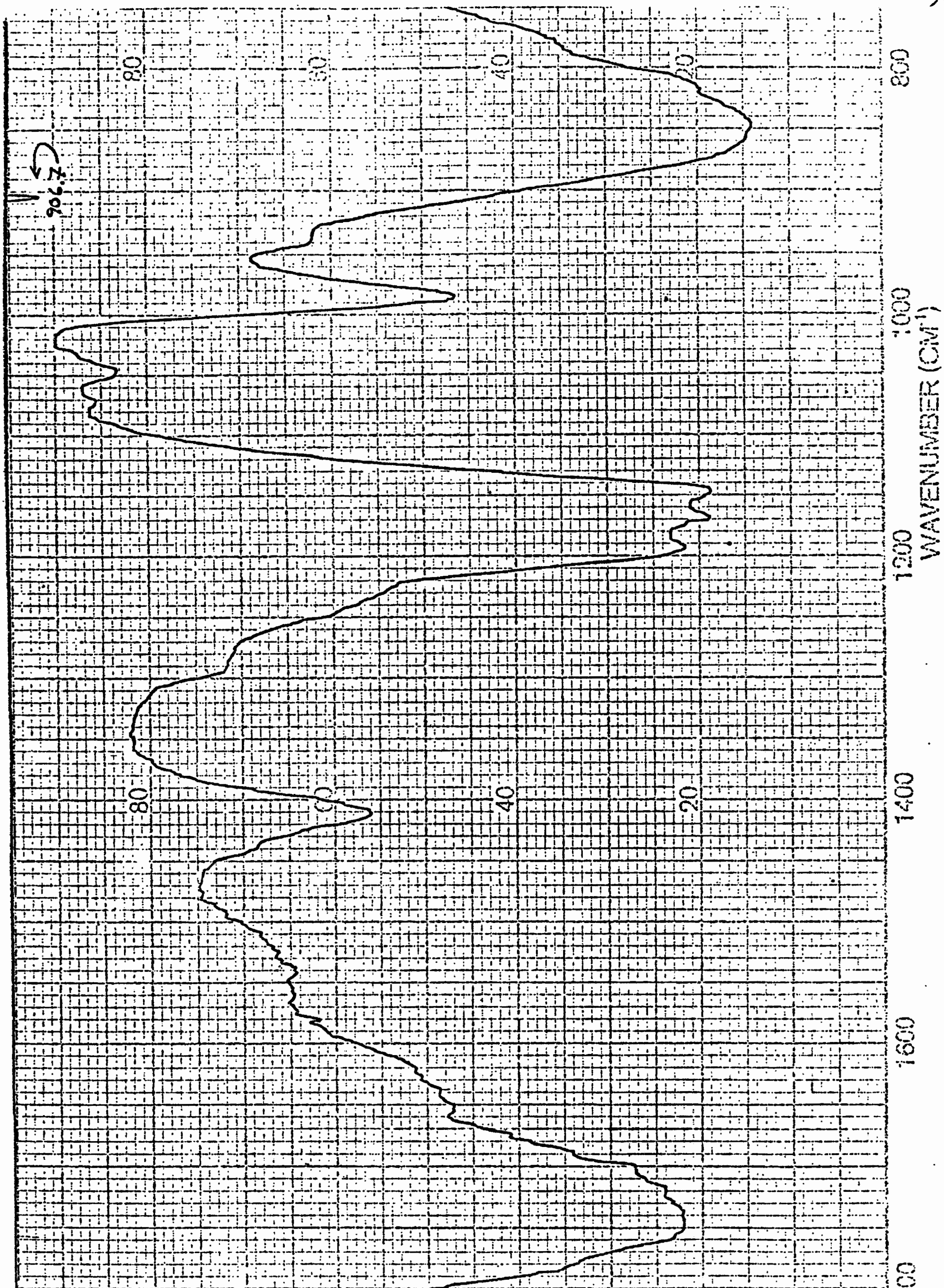
INFRARED SPECTRA OF PRODUCTS



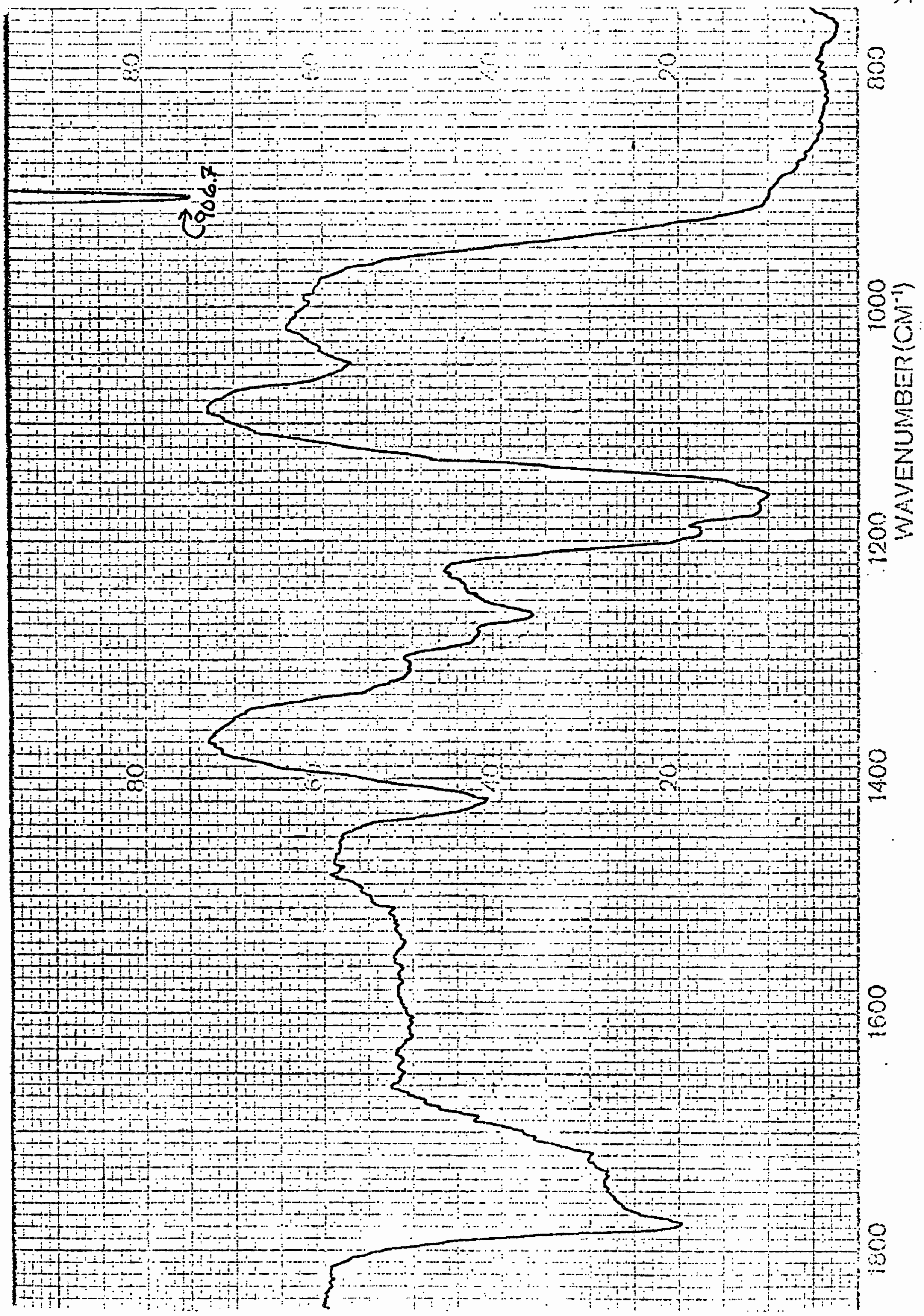
Infrared spectrum of $CrO_2((O_2C)_2(CF_2)_3)$, 1900 to 800 cm^{-1}, (KBr pellet).



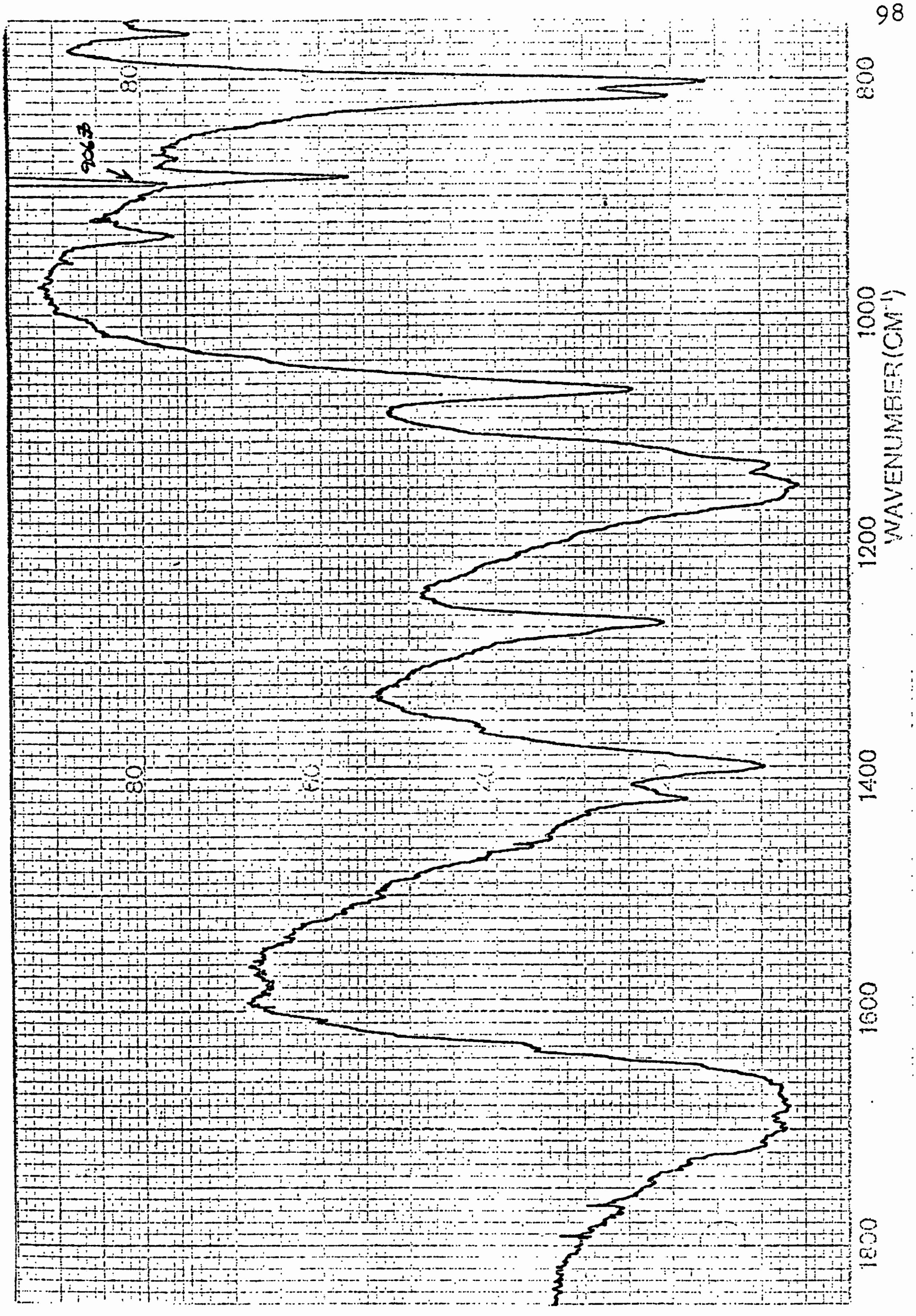
Infrared spectrum of $CrO_2((O_2C)_2(CF_2)_3)$, 1300 to 250 cm^{-1}, (KBr pellet).



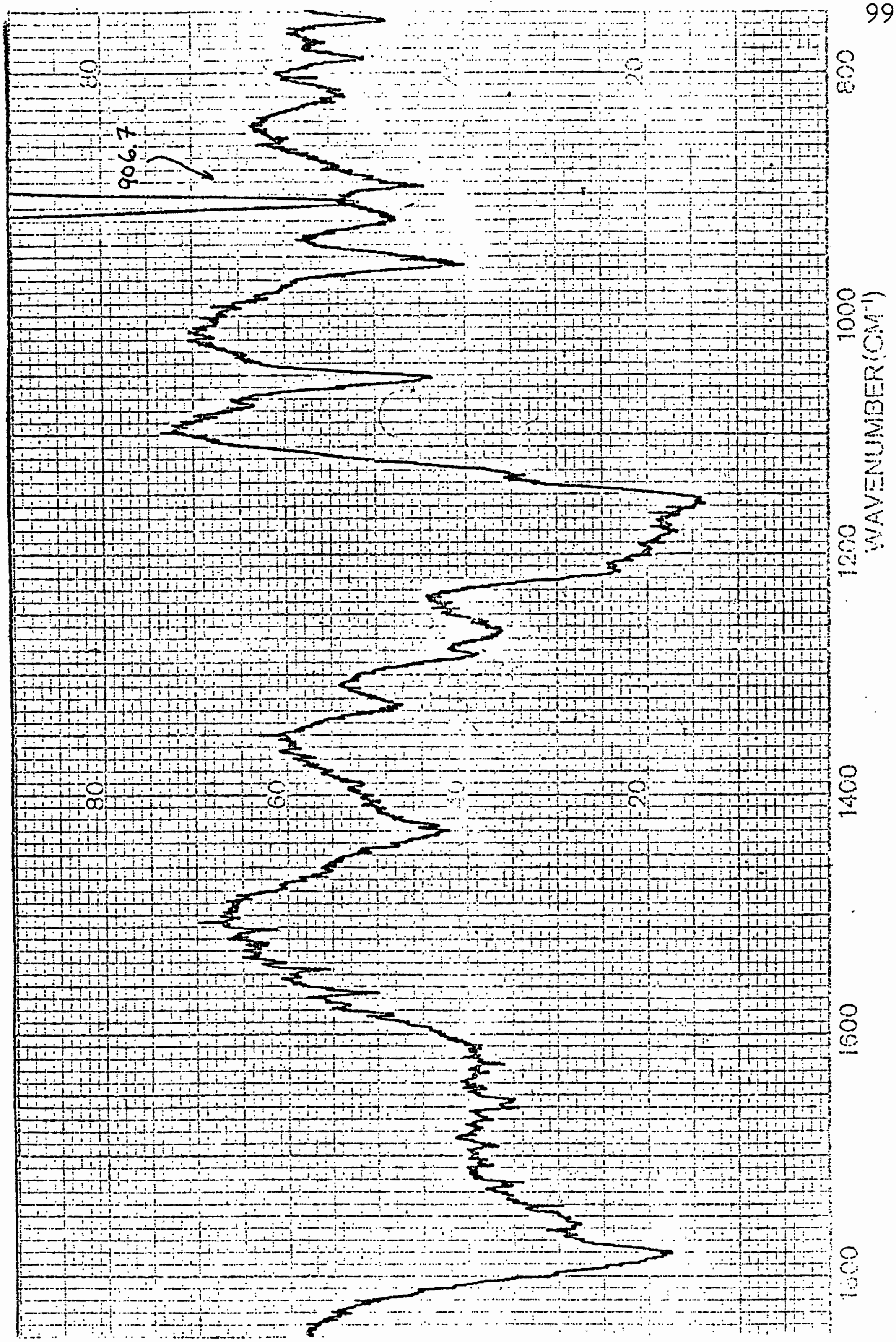
Infrared spectrum of $MoO_2((O_2C)_2(CF_2)_3)$, (KBr pellet).



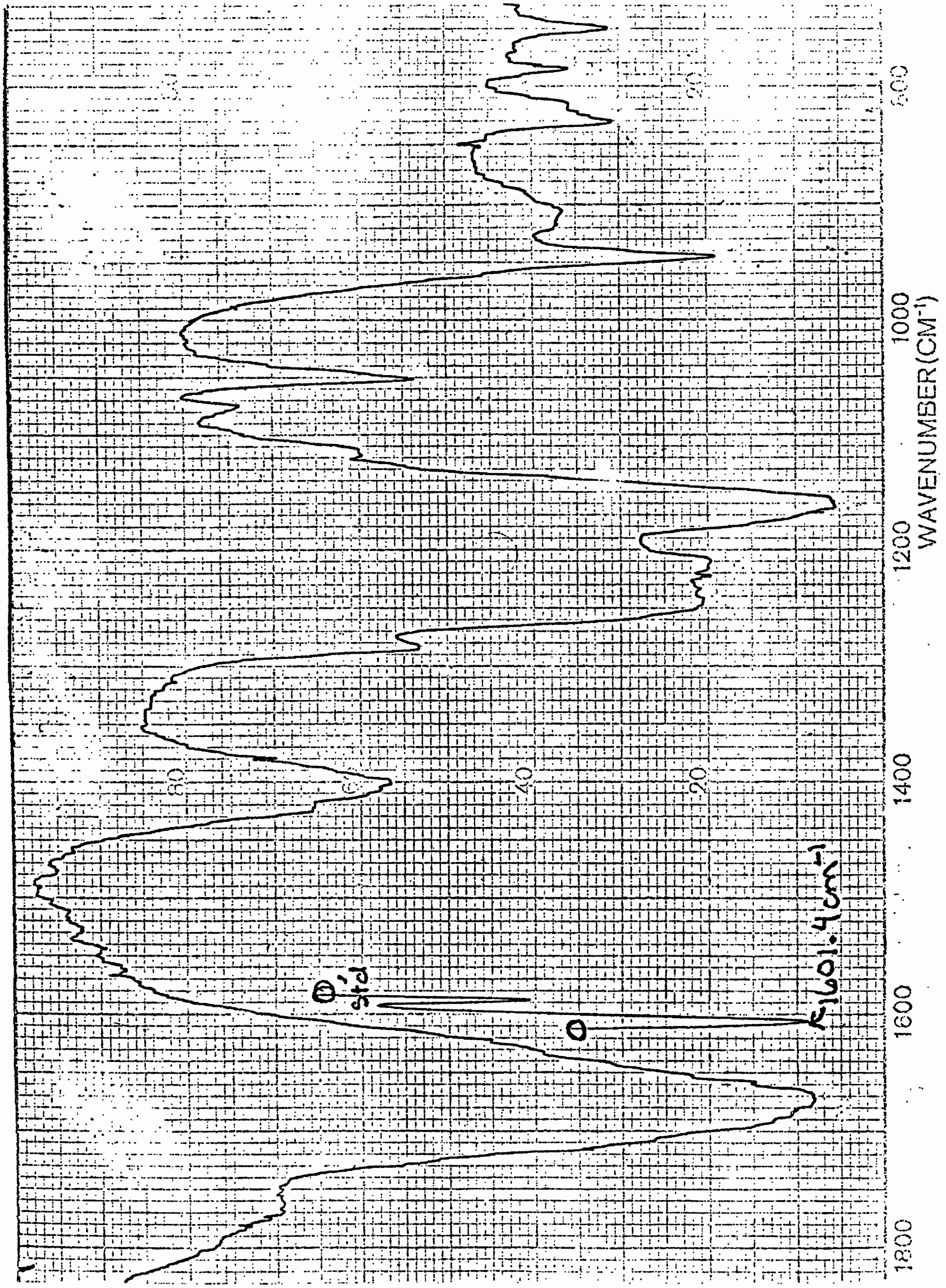
Infrared spectrum of $WO_2((O_2C)_2(CF_2)_3)$, (KBr pellet).



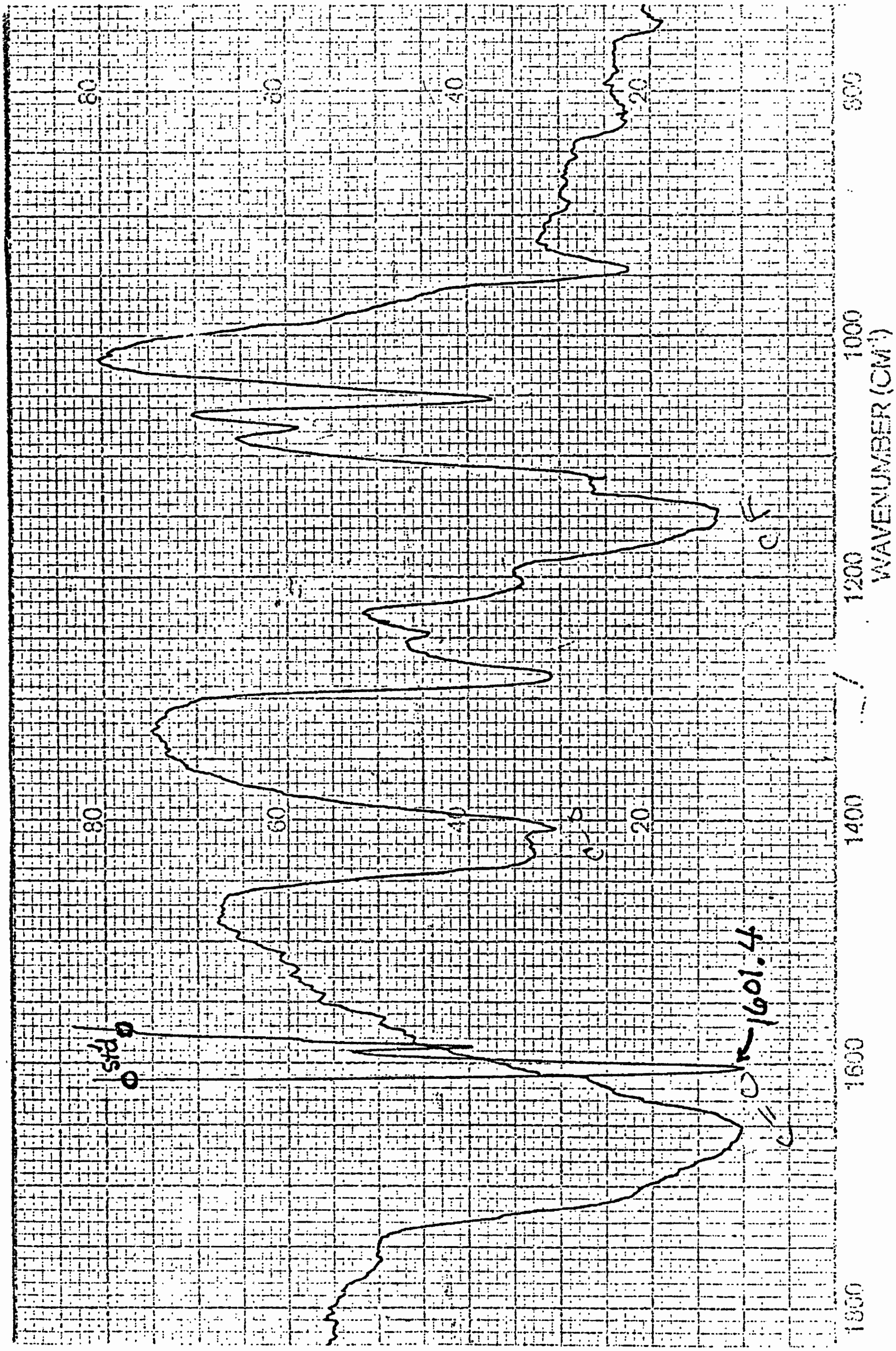
Infrared spectrum of $Na_2((O_2C)_2(CF_2)_3)$, (KBr pellet).



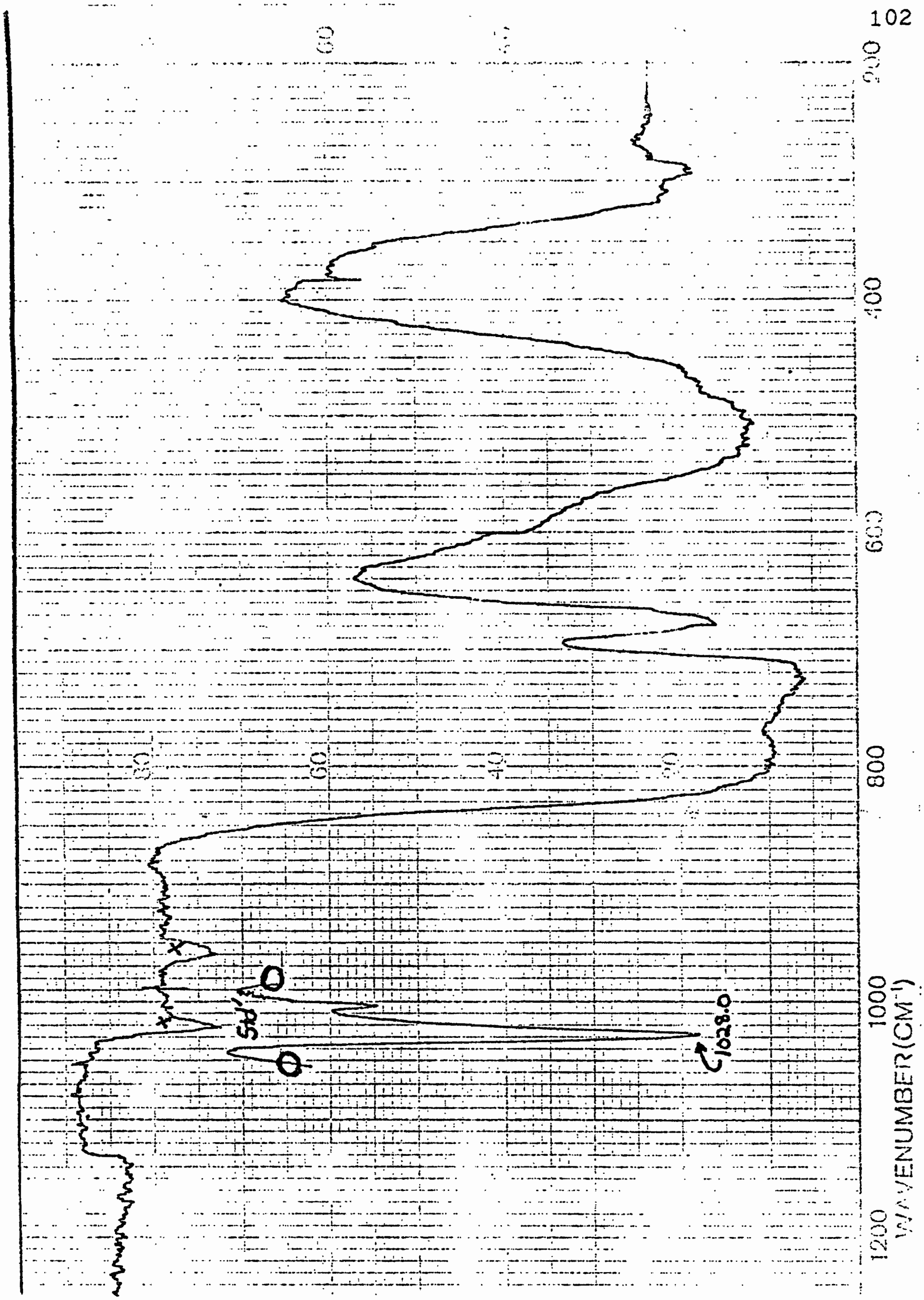
Infrared spectrum of $K_2CrO_2((O_2C)_2(CF_2)_3)_2$, (KBr pellet).



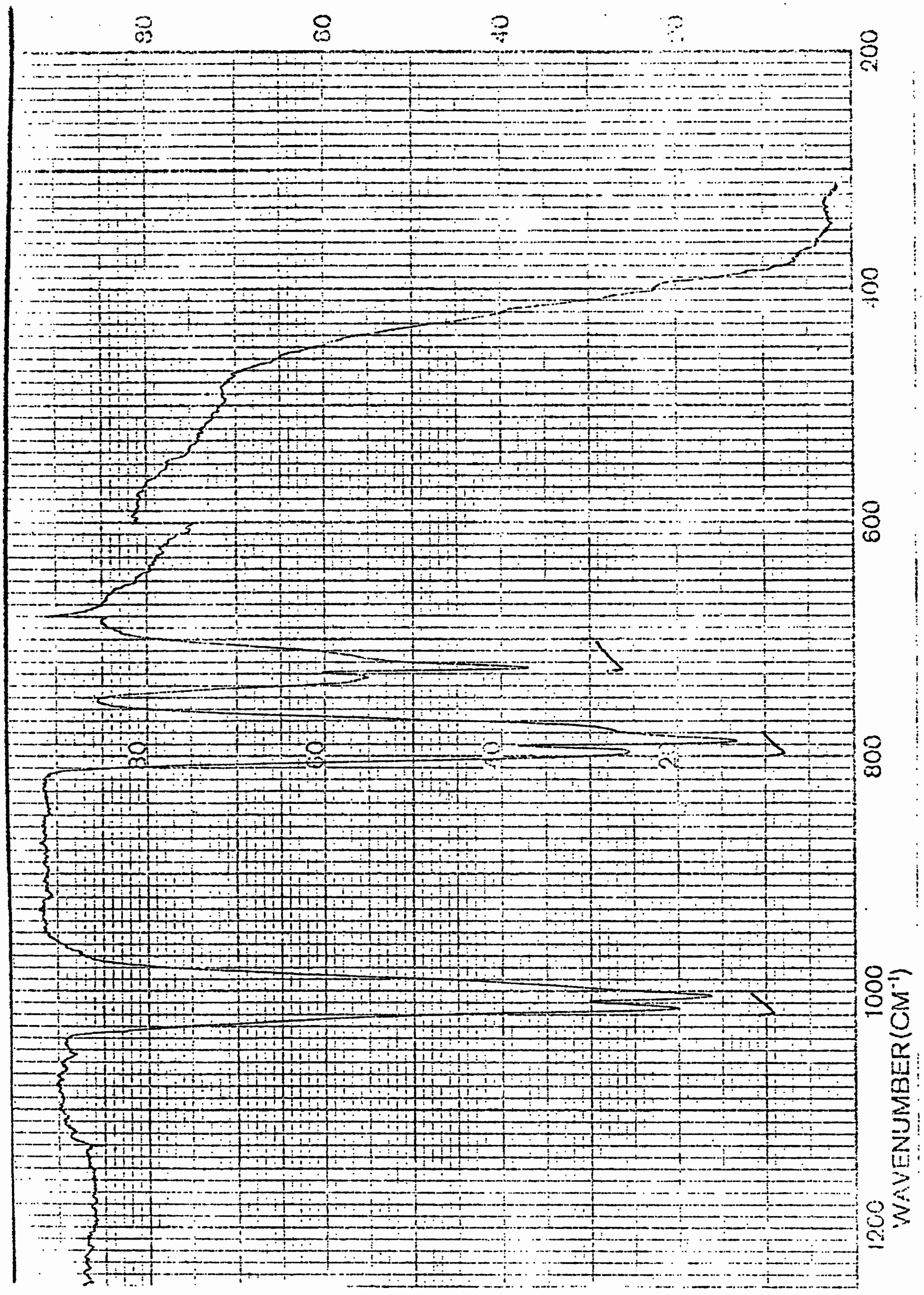
Infrared spectrum of $Na_2MoO_3((O_2C)_2(CF_2)_3)$, (KBr pellet).



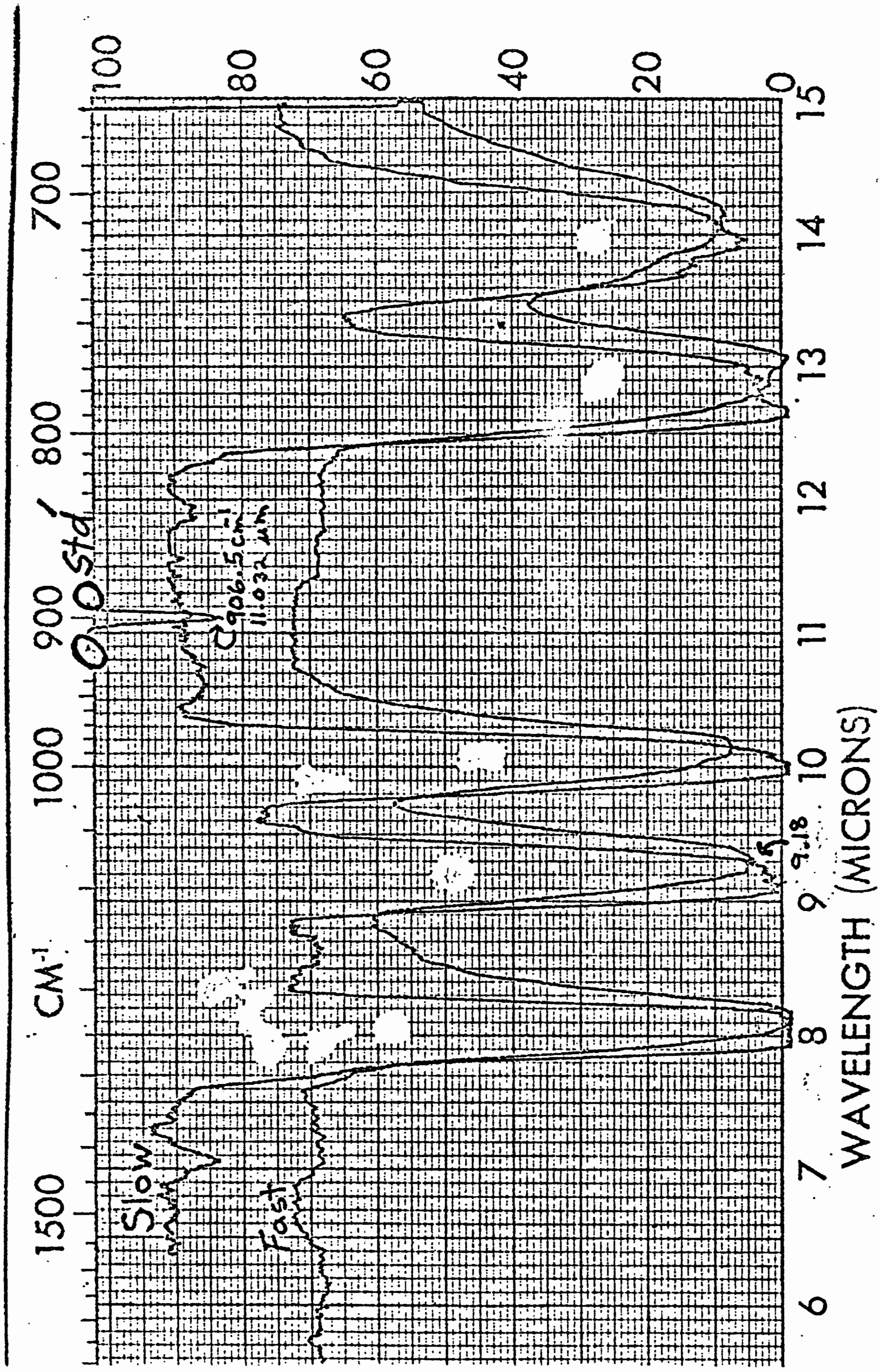
Infrared spectrum of $Na_2WO_3((O_2C)_2(CF_2)_3)$, (KBr pellet).



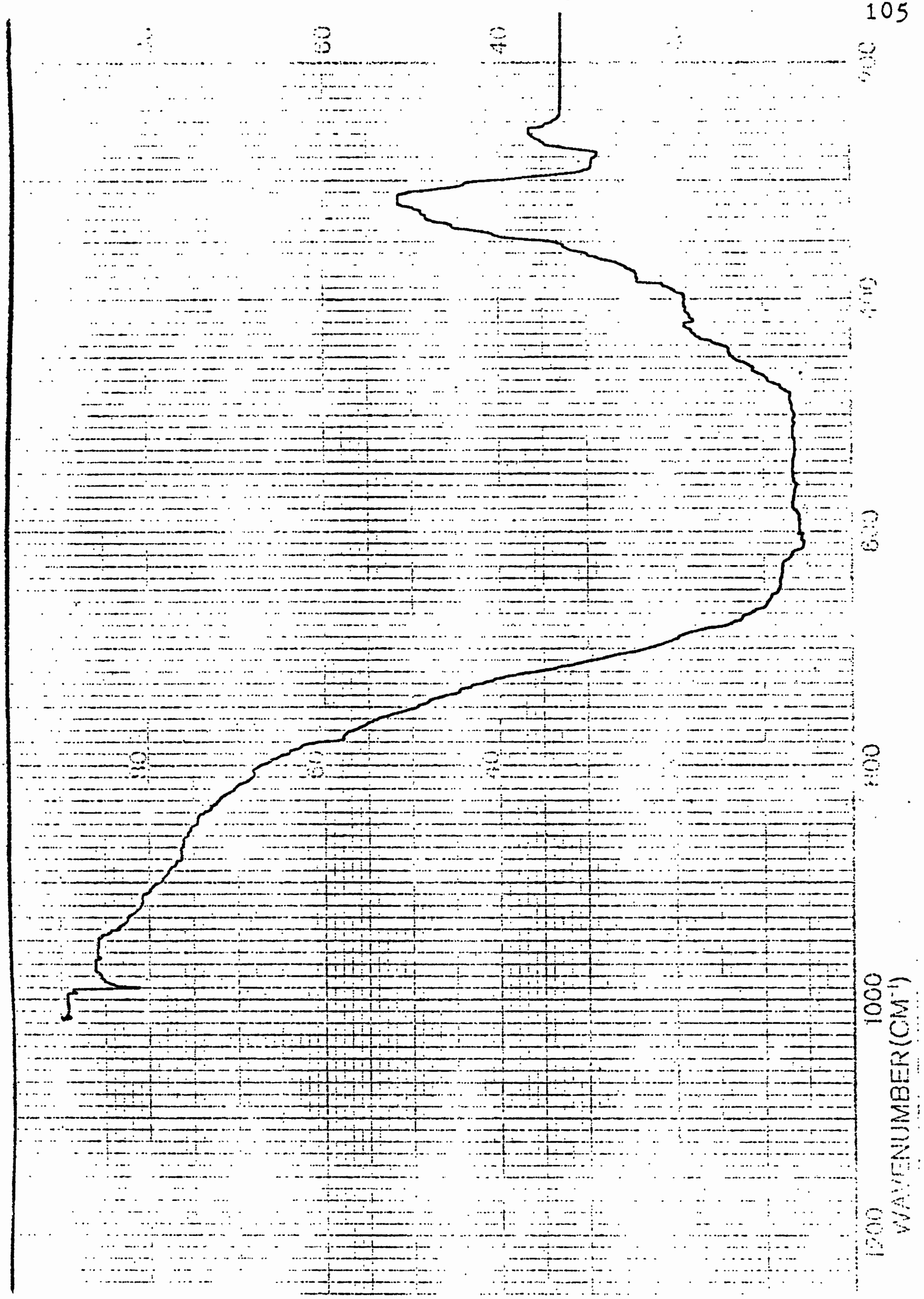
Infrared spectrum of CrF_5, (solid smear).



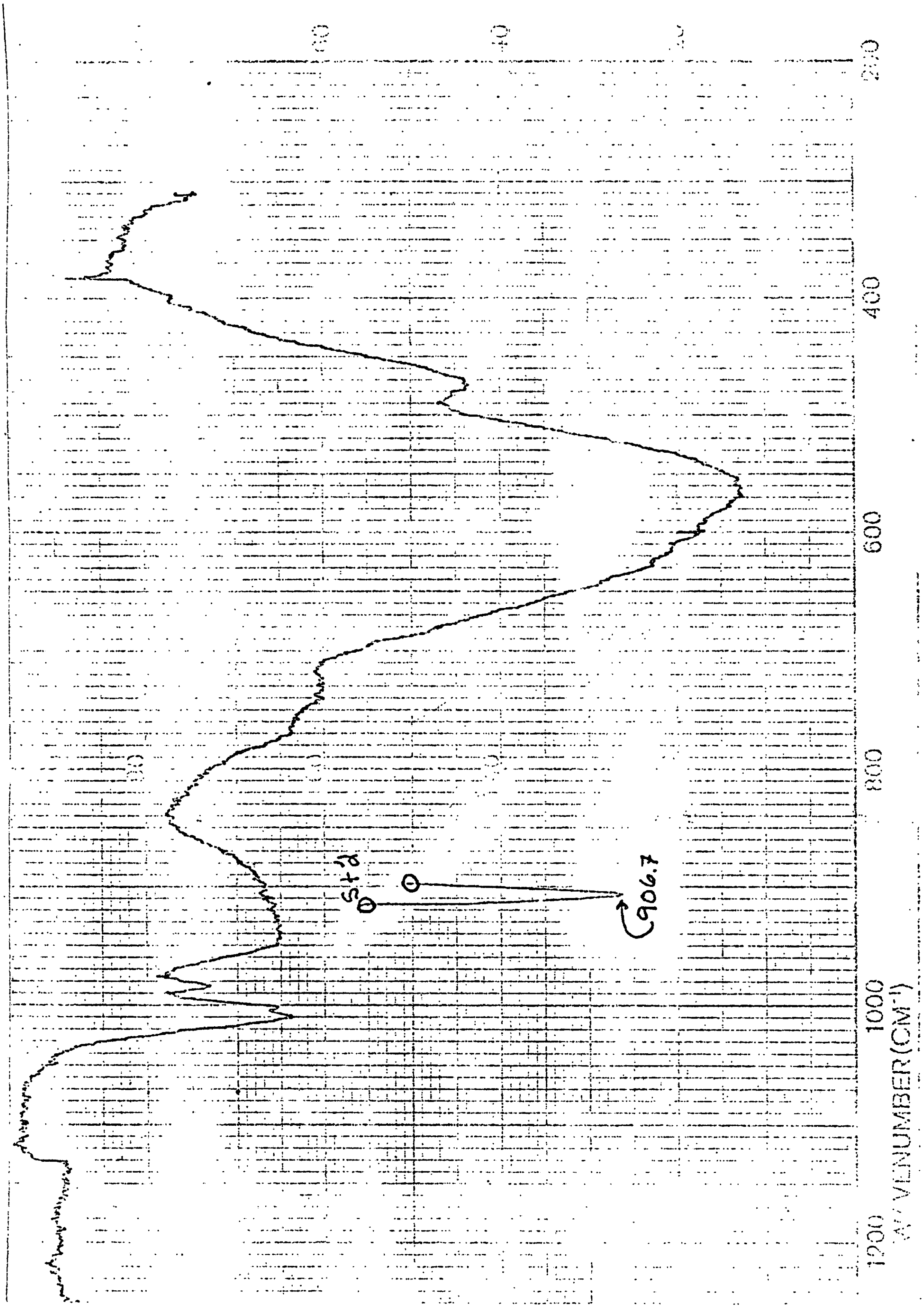
Infrared spectrum of CrO_2F_2, (gas phase, 10 mm Hg).



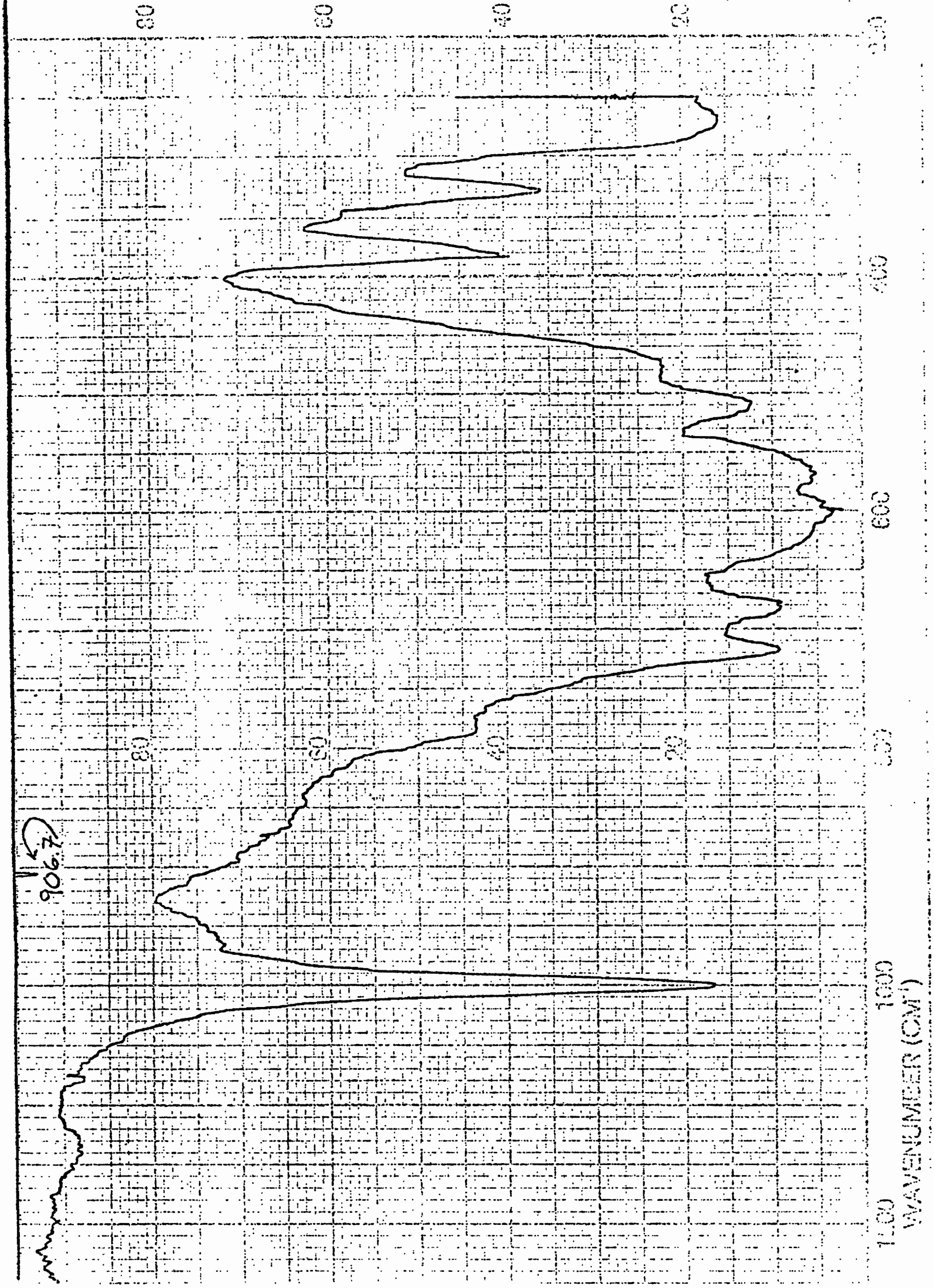
Infrared spectrum of the chromyl fluoride fluorination products, (gas phase).



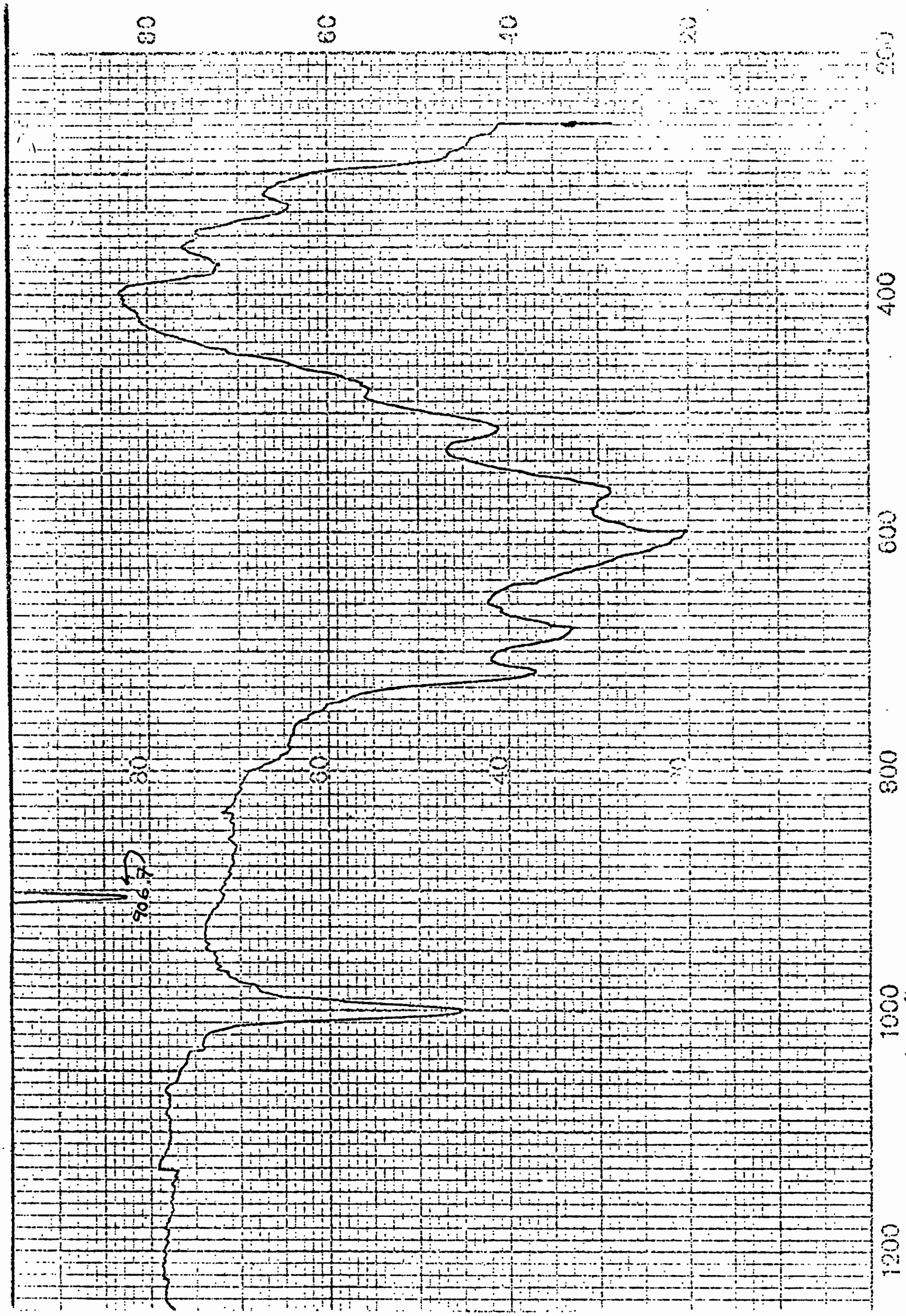
Infrared spectrum of CrF_3, (KBr pellet).



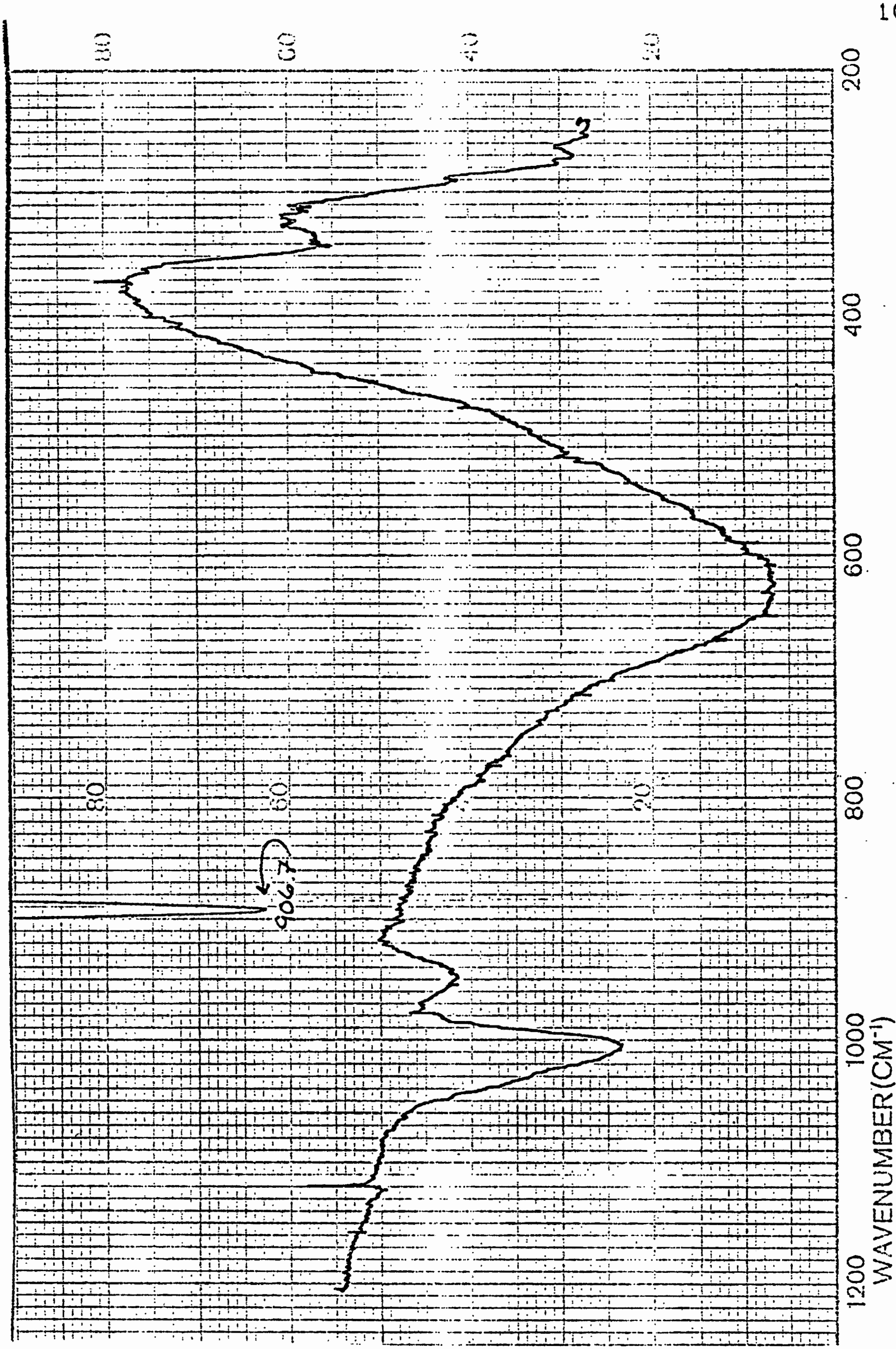
Infrared spectrum of $CrOF_2$, (KBr pellet).



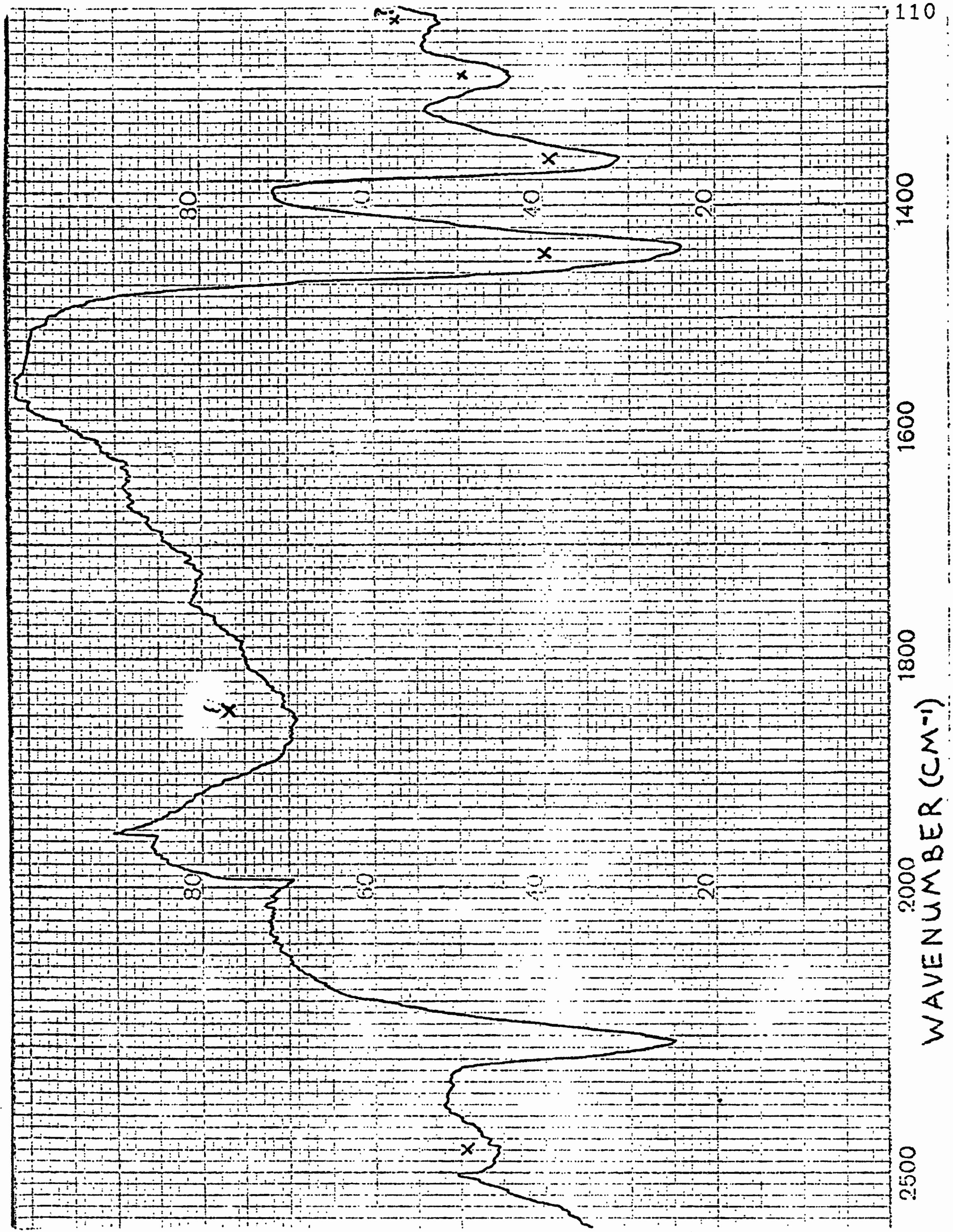
Infrared spectrum of $CrOF_3$, (KBr pellet).



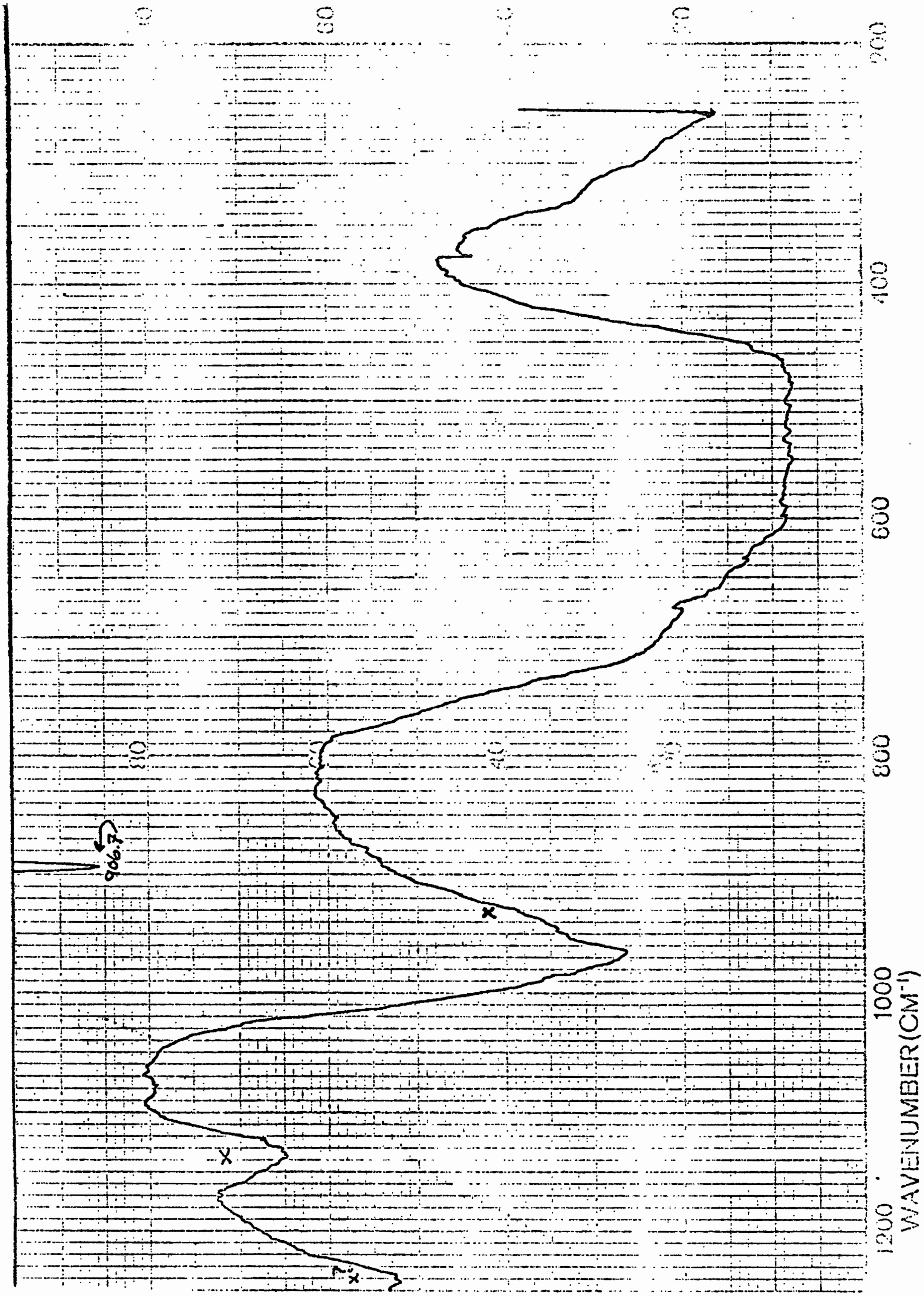
Infrared spectrum of $CrOF_3$, (KBr pellet).



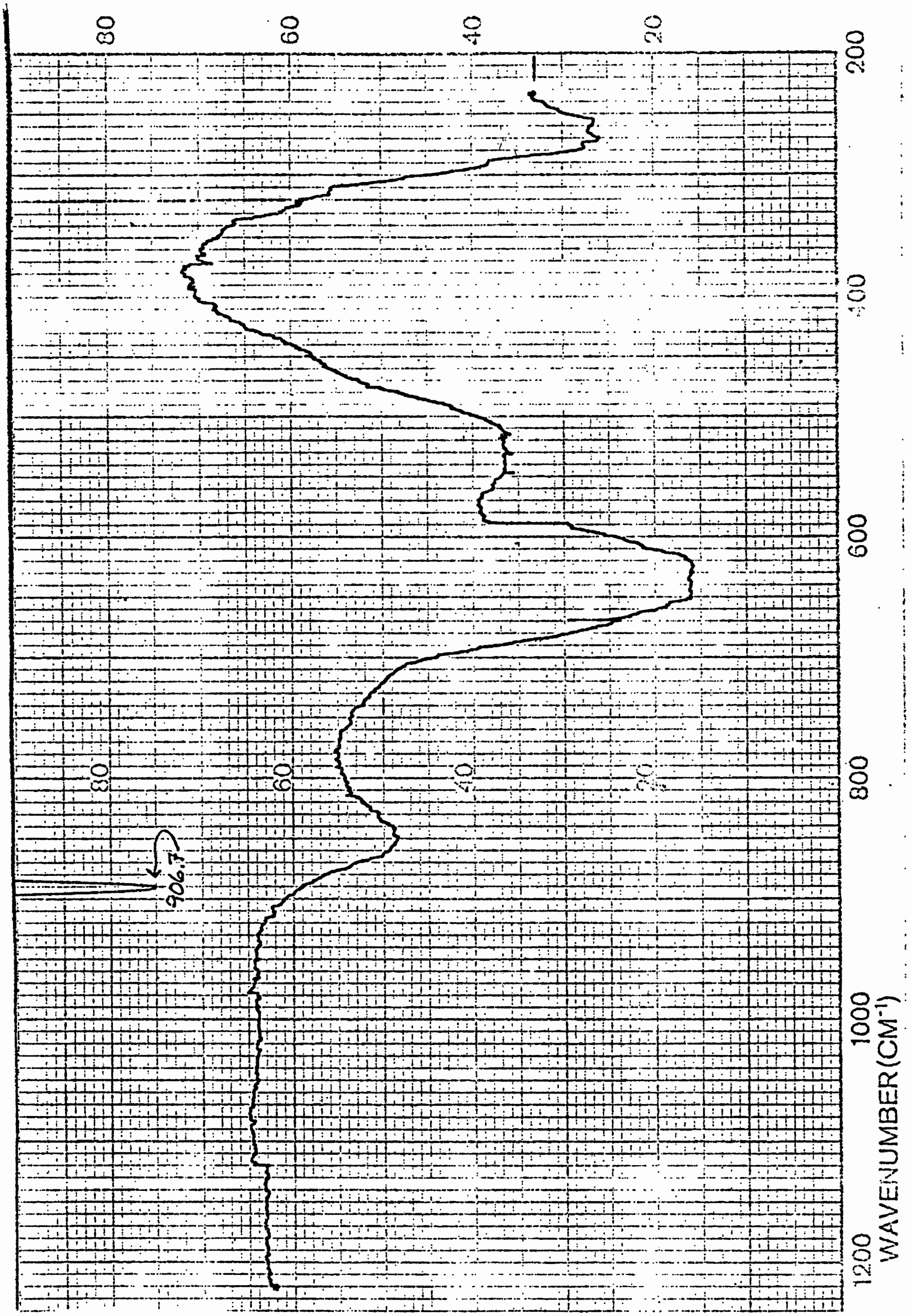
Infrared spectrum of $KCrOF_4$, (KBr pellet).



Infrared spectrum of NO_2CrOF_4, 2600 to 1250 cm^{-1}, (Nujol mull, x=Nujol).



Infrared spectrum of NO_2CrOF_4, 1250 to 250 cm^{-1}, (Nujol mull, x=Nujol).



Infrared spectrum of $CrF_2Sb_2F_{11}$, (KBr pellet).