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High Valent Chromium (V) and Chromium (VI) Complexes

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APPROVED BY MEMBERS OF THE THESIS COMMITTEE:

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A new preparative route to the only neutral chromium (V) oxide fluoride, chromium oxide trifluoride, has been accomplished by the reaction of xenon difluoride with chromyl fluoride at high temperature. The chromium oxide trifluoride is produced as crystals which are suitable for single crystal studies. In reactions of chromium oxide trifluoride with alkali and alkaline metal fluorides in anhydrous hydrogen fluoride, new chromium(V) oxide fluoride salts were obtained; these salts were not of high purity due to unknown problems. An attempt to prepare chromium oxide

tetrafluoride by the reaction of xenon difluoride with chromyl fluoride in anhydrous hydrogen fluoride failed to produce the desired product.

The new chromium(VI) complexes naphthyridinium chlorochromate (NapCC), pyrazinium chlorochromate (PzCC), pyrazinium-N-oxide chlorochromate (PzOCC), tripyridinium chlorochromate (TPCC), naphthyridinium dichromate (NapDC), pyrazinium trichromate (PzTC), and pyrazine chromium(VI) oxide (PzCA) were prepared; the chlorochromates were readily produced as orange crystalline products in 6M HCl, the dichromate and trichromate complexes were produced in distilled water as crystalline products, and the chromium (VI) oxide complex was produced by the inert atmosphere reaction of pyrazine and chromium trioxide in dichloromethane.

The chromium(VI) complexes NapCC, PzCC, PzOCC, TPCC, and NapDC were all studied as oxidizing agents for the oxidation of alcohols. Except for PzOCC, all of these complexes are milder oxidants than pyridinium chlorochromate (PCC), and NapDC is highly selective for the oxidation of benzyl alcohol.

HIGH VALENT CHROMIUM(V)
AND CHROMIUM(VI) COMPLEXES

by

HARRY BENNETT DAVIS

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

MASTER OF SCIENCE
in
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TO THE OFFICE OF GRADUATE STUDIES AND RESEARCH:

The members of the Committee approve the dissertation of Harry Bennett Davis presented May 17, 1984.

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TO MY GRANDMOTHER,

VERA ESTHER TUTHILL DAVIS

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CHAPTER I

INTRODUCTION

Purpose

The oxidation of organic molecules by hexavalent chromium reagents is a well recognized synthetic technique to the organic chemist. The main concern of current research in this area involves the preparation of hexavalent chromium species which are, (i) capable of producing high yields of a desired product in an oxidation reaction, (2i) stereoselective for a particular alcohol function in a multifunctional molecule, and (3i) are easily separable in the reacted and unreacted forms from the desired product; such reagents are particularly beneficial and necessary to the pharmaceutical industry where the effectiveness of a drug is often intimately dependant upon an exact molecular structure and geometry, one which is often derived from a multistep synthesis employing a multifunctional starting molecule. The cost effectiveness of producing such a highly specific molecule is therefore dependent upon the yield obtained of the desired product at each step in the synthetic pathway, requiring reagents which possess the characteristics mentioned above.

Chromium in the pentavalent state has long been postulated as an intermediate in the reduction of hexavalent chromium to trivalent chromium which occurs during oxidation reactions. Because there are not a great number of stable pentavalent chromium complexes known, and the use of such species as oxidizing agents has not been widely explored, the preparation, isolation, and characterization of new stable pentavalent chromium species may allow chemists the opportunity to more fully understand the role which pentavalent chromium plays in oxidation reactions. For example, it has not been unequivocally demonstrated whether or not pentavalent chromium undergoes a one electron reduction to tetravalent chromium, a concerted two electron reduction to trivalent chromium, or both during the reduction of hexavalent chromium to trivalent chromium.

In light of these important concerns, new pentavalent and hexavalent chromium complexes have been prepared. A new route to the only known stable neutral oxyfluoride of pentavalent chromium, $CrOF_3$, has been developed, and new hexavalent chromate complexes have been prepared and characterized. Most of the new chromate complexes show mild to moderate activity as oxidizing agents, while one of the new complexes has proven to be highly selective for the oxidation of specific alcohol functions.

Pentavalent Chromium Complexes

There are few known examples of neutral pentavalent chromium complexes, and as such, chromium doesn't exhibit such a broad range of stable oxidation states as found for molybdenum and tungsten.

Pentavalent chromium salts however have been known for nearly eighty years. For example, synthesis of $XCrOCl_4$ and X_2CrOCl_5 (X = unipositive cation) complexes was accomplished as early as 1906 (1). These were prepared by dissolving chromium trioxide in glacial acetic acid (saturated with HCl), and adding to that a glacial acetic acid solution containing the appropriate cation (also saturated with HCl)(2):

$$\text{I-1} \quad \underset{\text{Satd. in HCl}}{CrO_3 \text{ in glacial HOAc}} + \underset{\text{Satd. in HCl}}{\text{cation in glacial HOAc}} \rightarrow \underset{\text{Precip.}}{\text{Cr(V) Salt}}$$

A number of oxotetrachloro and oxopentachloro pentavalent chromium salts have been prepared using this method, and a large number of publications on the spectroscopic properties have appeared in the literature during the last 25 years (3, 4); these d^1 complexes continue to be the subject of recent research interests (5).

Pentavalent chromium oxide fluoride salts are not nearly as well known as the oxide chloride salts. Up to 1970, only three such salts were known. The potassium (5), silver (6), and triethylamonium (3) salts were obtained as in equations 2, 3, 4, and 5:

I-2 $CrO_3 + BrF_3 + KCl \longrightarrow KCrOF_4$

I-3 $K_2Cr_2O_7 + BrF_3 \longrightarrow 2KCrOF_4$

I-4 $Ag_2Cr_2O_7 + BrF_3 \longrightarrow 2AgCrOF_4$

I-5 $(Et_4N)_2CrOCl_5 + AgF \xrightarrow[CH_2Cl_2]{HF} AgCl + (Et_4N)_2CrOF_5$

These remain the only examples of chromium(V) oxide fluoride salts known.

Although most oxohalo pentavalent chromium salts are immediately hydrolyzed upon exposure to moisture, there are several examples of pentavalent chromium salts which are not hydrolyzed by water, even upon dissolving in water. The potassium bis (2-hydroxy-2-methylbutyrato)oxochromate(V) salt is reportedly soluble in water without decomposition (8), and the bis(perfluoropinacol)oxochromate(V) salt is reportedly insoluble in water (9). In general, Rocek and co-workers have shown that tertiary x-hydroxy acids form complexes with chromium(V) which are stable in aqueous solutions for prolonged periods of time, and can be isolated in solid form (10). These highly stable chromium(V) salts all have in common a ligand system which is rich in electrons and stabilizes the pentavalent state towards disproportionation.

There are only three known examples of neutral pentavalent chromium complexes; they are, chromium pentafluoride (CrF_5), chromium oxide trichloride ($CrOCl_3$), and chromium oxide trifluoride ($CrOF_3$).

Chromium pentafluoride has been known for over 40 years (11). It is obtained by the high temperature, high pressure, static fluorination of chromium trifluoride (12):

I-6 $CrF_3 + F_2 \longrightarrow CrF_5$

It can also be prepared by the stepwise replacement of oxygen in the high temperature fluorination of chromium trioxide (13), or by the direct fluorination of chromium metal at elevated temperatures (14):

I-7 $2CrO_3 + 5F_2 \longrightarrow 2CrF_5 + 3O_2$

I-8 $2Cr + 5F_2 \longrightarrow 2CrF_5$

Chromium pentafluoride is a stable crimson colored solid which is volatile at room temperature.

Chromium oxide trichloride was first prepared by the reactions of CrO_3 with either thionyl chloride or sulfuryl chloride at low temperature (15):

I-9 $CrO_3 + SOCl_2 \xrightarrow{0°C} CrO_2Cl_2 + SO_2$

$CrO_2Cl_2 + SOCl_2 \longrightarrow CrOCl_3 + SO_2 + \frac{1}{2}O_2$

I-10 $CrO_3 + SO_2Cl_2 \xrightarrow{0°C} CrO_2Cl_2 + SO_3$

$CrO_2Cl_2 + SO_2Cl_2 \longrightarrow CrOCl_3 + SO_3 + \frac{1}{2}O_2$

The isolated yield of $CrOCl_3$ from these reactions was only two percent, the major product being the hexavalent CrO_2Cl_2. In later work, Johannesen and Krauss were able to improve the yield of $CrOCl_3$ to fifty percent by the reaction of CrO_2Cl_2 with BCl_3 (16):

I-11 $CrO_2Cl_2 + 2/3BCl_3 \longrightarrow CrOCl_3 + 1/3B_2O_3 + \frac{1}{2}Cl_2$

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

Impure chromium oxide trifluoride was first prepared by Sharpe and Woolf by the reaction of CrO_3 with BrF_3 (6); the product obtained contained bromine which could not be removed even by heating the solid at 200°C under vacuum. Later efforts by Clark and Sadana to prepare pure $CrOF_3$ by reacting BrF_3, BrF_5, and ClF_3 with CrO_3 and CrF_4 (BrF_3 only) produced a solid product which could not be freed of the interhalogen fluorinating agent (17). Pure $CrOF_3$ was first prepared by Green et al., by heating ClF and CrO_3 to 120°C for 4 hr (18). The crude $CrOF_3$ obtained contained chlorine which was removed by repeated heating to 120°C in a static fluorine atmosphere. Pure $CrOF_3$ was thus obtained as a purple solid which is stable up to 300°C; spectroscopic and physical evidence indicate a polymeric structure with extensive fluorine bridging. The chemistry of this unusual chromium(V) species remains largely unexplored. The reaction of KF with $CrOF_3$ in anhydrous HF produces the well known $KCrOF_4$ (18)

I-12 $CrOF_3 + KF \xrightarrow[AHF]{} KCrOF_4$

while the reaction of NO_2F with $CrOF_3$, run neat at 50°C, appears to produce NO_2CrOF_4 (19):

I-13 $CrOF_3 + NO_2F \xrightarrow[50°C]{} NO_2CrOF_4$

A new method of preparing highly pure crystalline $CrOF_3$, and some chemistry of $CrOF_3$ are the subjects of Chapter III.

Hexavalent Chromium Complexes

Compared to pentavalent chromium complexes, there are a large number of stable hexavalent chromium complexes known. Of primary concern here are the chromium(VI) species chromium trioxide (CrO_3), chromyl chloride (CrO_2Cl_2), and chromyl fluoride (CrO_2F_2), from which the forementioned pentavalent chromium complexes are derived; and the complexes $LCrO_3Cl$ and $L_2Cr_2O_7$ (L = unipositive cation) which are formed by the aqueous equilibrium of chromium trioxide in the presence of a base L, and chloride ion in the case of CrO_3Cl^-. There are also examples of neutral complexes of chromium trioxide, which, analogous to the neutral pentavalent chromium complexes, tend to be somewhat moisture sensitive, and thus are more difficult to handle than the salt complexes. All of these chromium(VI) complexes are potentially useful as oxidizing agents.

Chromyl chloride is the best known oxide halide of chromium(VI); it has been known for at least 160 years (20). There are several methods by which chromyl chloride can be made (21); the most common route seems to be the reaction of chromium trioxide or dichromate with hydrochloric acid in the presence of a dehydrating agent (22):

I-14 $CrO_3 + HCL \xrightarrow{\text{Conc. } H_2SO_4} CrO_2Cl_2$

I-15 $Cr_2O_7 + HCl \xrightarrow{\text{Conc. } H_2SO_4} 2CrO_2Cl_2$

Chromyl chloride is a strong oxidizing agent which ignites many organic compounds (23). The oxidizing strength of chromyl chloride can be modified by adsorbing it onto silica-alumina gel; under these conditions the chromyl chloride effectively converts alcohols to only the aldehyde and ketone forms, and not to the acids (24). The use of chromyl chloride as an oxidizing agent, particularly for the oxidation of carbon carbon double bonds continues to be of interest (25).

Chromyl fluoride is a strongly oxidizing species which is likely not useful as a homogeneous species for oxidations in most organic reactions; due to its strength as an oxidant, it could not be expected to be selective, and would probably destroy many organic molecules. Many reports have appeared on the preparation of chromyl fluoride (26). The most recent report by Green and Gard involves (among others) the use of chlorine monofluoride to fluorinate chromyl chloride, or tungsten hexafluoride to fluorinate chromium trioxide (27):

I-18 $CrO_2Cl_2 + ClF \xrightarrow{-78°C} CrO_2F_2 + 2Cl_2$

I-19 $CrO_3 + WF_6 \xrightarrow{125°C} CrO_2F_2 + WOF_4$

These reactions produce chromyl fluoride in quantitative yields as a dark violet-red solid which is volatile at room temperature, and thermally stable up to 500°C.

Of all the hexavalent chromium complexes known, the dichromates, the neutral chromium trioxide complexes, and more recently the chlorochromates, are the most widely used for the oxidation of alcohols to carbonyl compounds. The oxidation of alcohols by hexavalent chromium involves a two electron oxidation of an alcohol, accompanied by a three electron reduction of chromium from the hexavalent to the trivalent state:

I-18 $2Cr(VI) + 3ROH \longrightarrow 2Cr(III) + 3RCOR'$

R' = H, aklyl, aryl, other

Sodium and potassium dichromates have long been used as oxidizing agents in organic chemistry. These dichromate complexes are strong oxidizing agents, and as such they provide little, if any, degree of selectivity; this therefore prevents the use of these complexes for the oxidation of any molecules which contain easily oxidizable substituents other than the one of primary interest.

One of the first examples of a mildly oxidizing hexavalent chromium complex was that of dipyridine-chromium(VI) oxide (28), and in pyridine (29) for the oxidation of secondary alcohols to ketones (30). Work done by Collins, using dichloromethane rather than pyridine as the solvent, showed that dipyridine-chromium(VI) oxide nearly quantitatively converted most primary and secondary alcohols tested to only the aldehydes and ketones, respectively (31). The use of dichloromethane as the solvent resulted in the easy isolation of the desired organic product due to the oxidized and reduced forms of the chromate complex remaining insoluble in this solvent. A disadvantage of dipyridine-chromium(VI) oxide, now commonly known as the "Collins Reagent," is that its preparation is somewhat tedious, requiring the use of inert atmosphere techniques; the complex itself is somewhat moisture sensitive as well.

The introduction of the pyridinium chlorochromate complex (PCC) as an oxidizing agent by Corey and Saggs was the first example of a mild chromium(VI) oxidant which, (i) can be easily prepared and isolated, (2i) can be stored for long periods of time, (3i) is nonhygroscopic, (4i) is insoluble in dichloromethane in its oxidized and reduced forms, and (5i) converts primary and secondary alcohols to aldehydes and ketones in good yields when used in only 1:1 stoichiometric quantities with alcohols (32). The complex is prepared from chromium trioxide, pyridine, and aqueous hydrochloric acid as in equation 20:

I-19 $CrO_3 + C_5H_5N + HCl \xrightarrow[H_2O]{} C_5H_5NH^+CrO_3Cl^-$

Although PCC is a milder oxidant than sodium or potassium dichromate, and produces carbonyl compounds in good yields, it does not preferentially oxidize specific alcohols (i.e. primary, secondary, benzylic, and allylic alcohols are not separately distinguished) and the need remains for selective oxidants.

Since the report of the now well known PCC, several other chlorochromate and dichromate complexes having different heterocyclic cations have been reported. The pyridinium dichromate complex is easily prepared by the aqueous reaction of pyridine and chromium trioxide (33):

I-20 $2C_5H_5N + CrO_3 \longrightarrow [C_5H_5NH]_2^{+}[Cr_2O_7]^{2-}$

The bipyridinium chlorochromate complex is formed in an analogous fashion to the pyridinium chlorochromate complex, while the bipyridine-chromium oxide complex is formed analogously to the dipyridine-chromium(VI) oxide complex (34). Quite recently the 4-(dimethylamino)pyridinium chlorochromate complex (35), as well as our own naphthyridinium and pyrazinium chlorochromate complexes (36) have been introduced as new, mild oxidants. The preparation and characterization of new chlorochromate, dichromate, trichromate, and chromium(VI) oxide complexes, and studies of the abilities of these new complexes to oxidize alcohols are the subjects of Chapters IV and V.

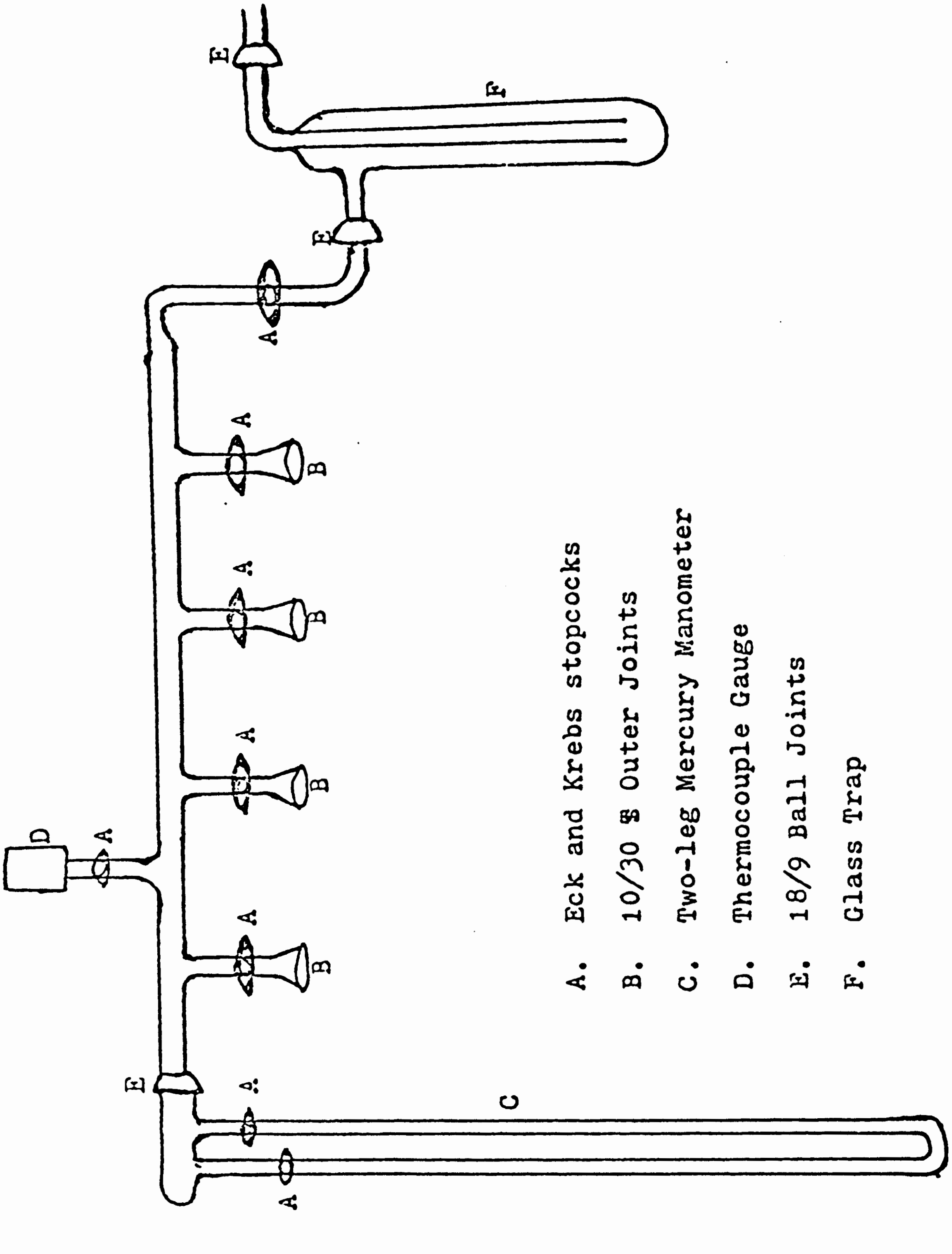
CHAPTER II

EXPERIMENTAL METHODS

Apparatus

Vacuum Systems. For most routine operations requiring the use of a high vacuum, or inert atmosphere conditions, a glass vacuum line was employed. The manifold was fabricated from 20 mm O.D. Pyrex glass tubing and fitted with four Eck and Krebs 2 mm high-vacuum stopcocks; outer standard taper 10/30 $\$$ ground glass joints were attached to the stopcocks. A two leg mercury manometer constructed of 10 mm O.D. Pyrex tubing was attached to the manifold by a ground-glass ball and socket joint. A Sargent-Welch Duo-Seal, Model 1400, rotary vacuum pump was used to achieve pressures down to $1x10^{-3}$ torr on a routine basis, and a Pyrex glass trap cooled to -196°C was interspaced between the manifold and the vacuum pump to freeze out any condensible gases. High vacuum pressures were measured with a Televac thermocouple gauge; a diagram of this vacuum line is shown in Figure 1.

A metal vacuum line constructed of ¼ in. O.D. copper tubing was employed for manipulation of gaseous materials which would attack Pyrex glass. Three Whitey brass valves with 10/30 $\$$ outer metal joints were attached to the mani-



A. Eck and Krebs stopcocks

B. 10/30 ₷ Outer Joints

C. Two-leg Mercury Manometer

D. Thermocouple Gauge

E. 18/9 Ball Joints

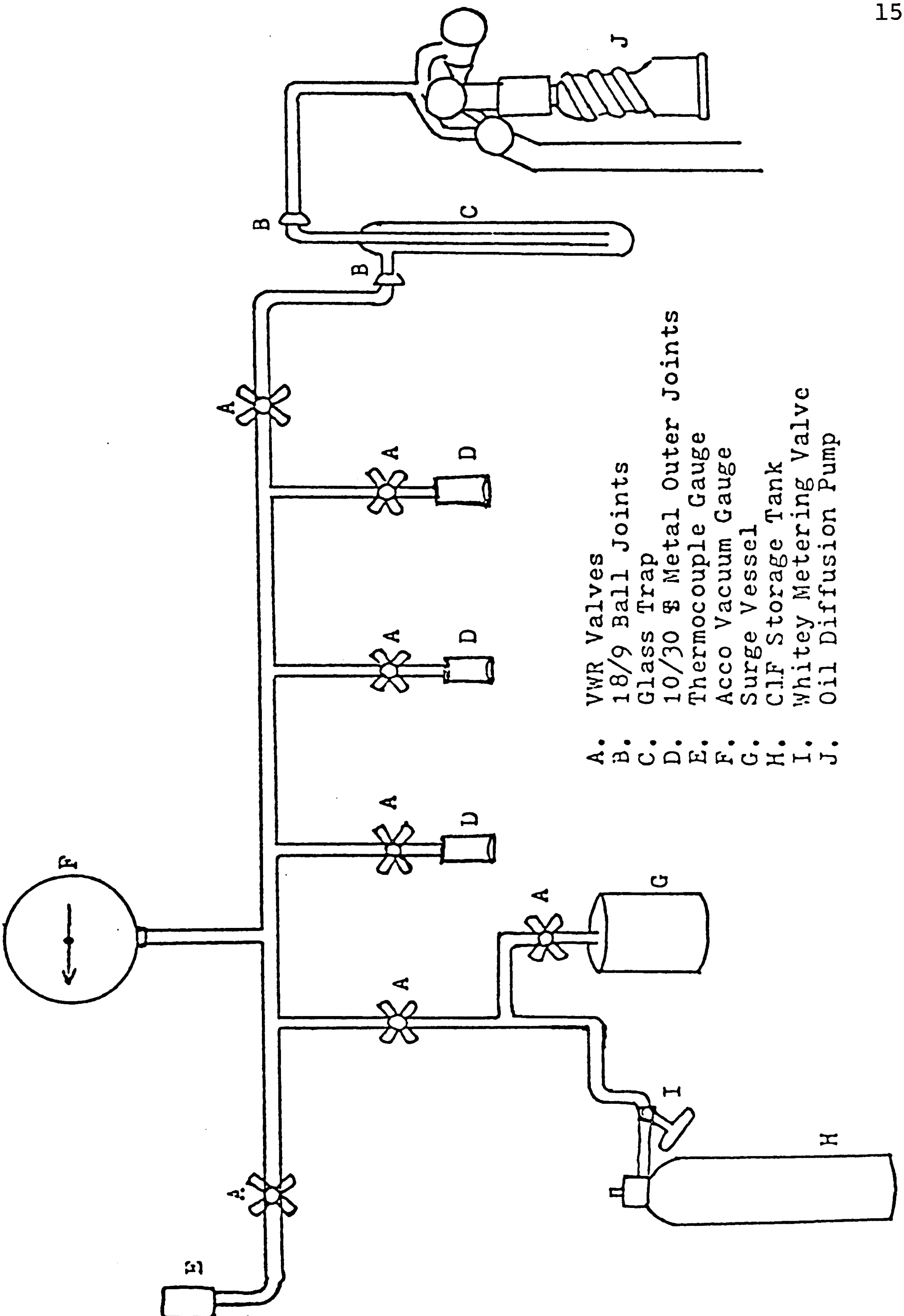
F. Glass Trap

Figure 1. Glass vacuum manifold

fold via Swagelok fittings. The metal line also featured a 1.8 liter copper expansion vessel, attached via Swagelok fittings, a Kontes thermocouple vacuum gauge, and an Acco diaphragm type gauge to measure pressures between 1 and 760 mmHg. A Pyrex glass trap cooled to -196°C was interspaced between the manifold and a Sargent-Welch Duo Seal, Model 1400, vacuum pump to collect condensible gases. This line routinely achieved a vacuum of $1\text{x}10^{-3}$ torr; a diagram of this vacuum line is shown in Figure 2.

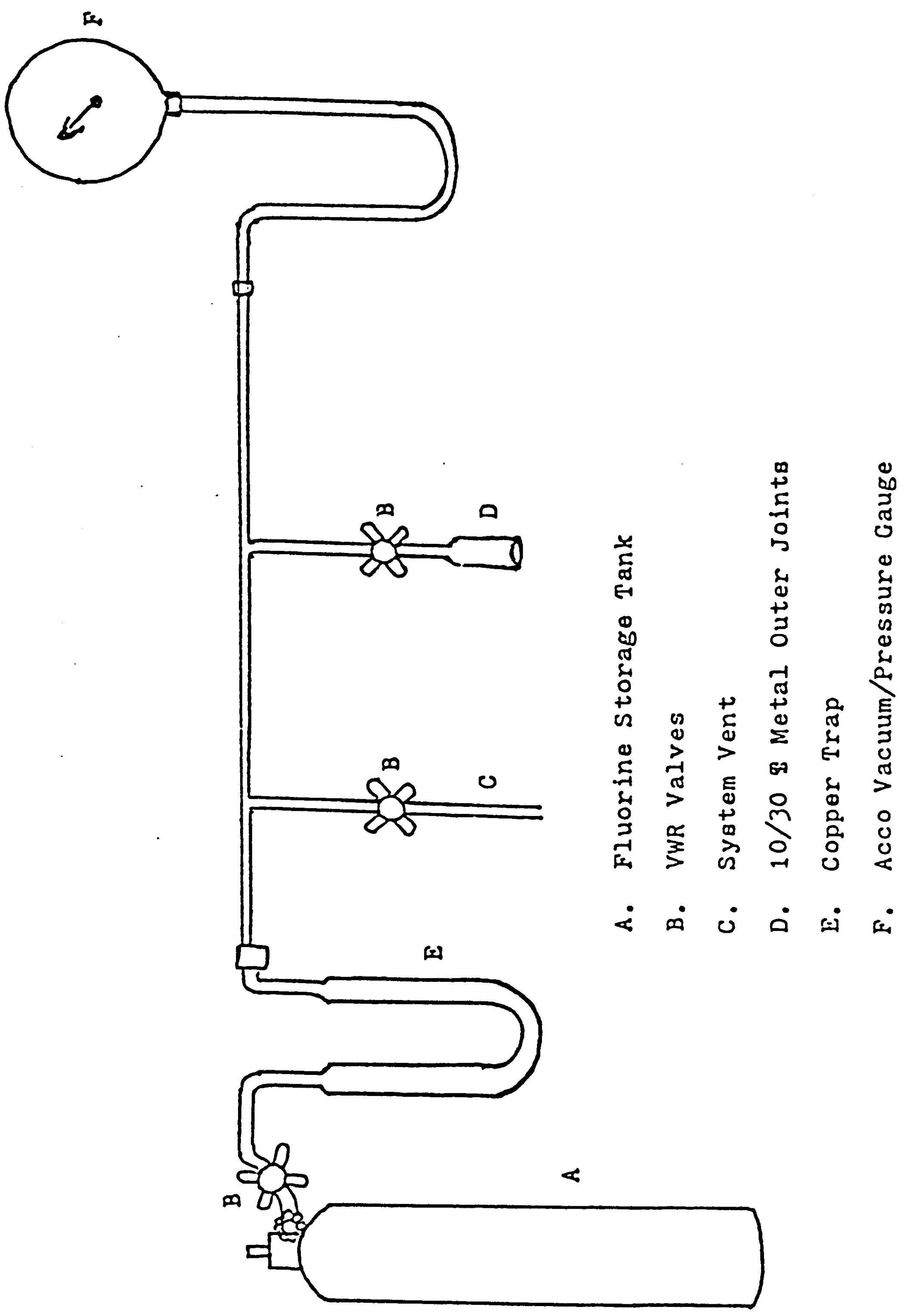
Fluorine Line. Elemental fluorine was transferred in a manifold constructed of ¼ in. O.D. copper tubing, to which one VWR valve and one Whitey brass valve were attached. One valve terminated in an outer 10/30 ₷ brass joint, while the other terminated in ¼ in. copper tubing and was used as a venting outlet. A U-tube constructed of ½ in. O.D. copper tubing was fitted on the line between the fluorine tank and the manifold; the U-tube was cooled to -78°C during fluorine transfers to remove some HF present as an impurity (P_{HF}(-78°C) < 5 mm). The fluorine tank was connected directly to the line by Swagelok fittings, and an Acco diaphragm type vacuum pressure gauge was used to measure pressures up to 760 mm Hg; a diagram of this line is shown in Figure 3.

Glass Vacuum Traps. For removal of volatile substances from a reaction, a Pyrex glass trap cooled to -196°C was



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 2. Metal vacuum system



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

Figure 3. Fluorine line

placed between the reaction vessel and the vacuum line; this prevented any volatile materials from contaminating the vacuum line, while collecting the materials at the same time for further characterization. A typical trap consisted of an outer tube of 20 mm I.D. Pyrex glass to which a Kontes high vacuum Teflon valve was attached via 8 mm I.D. Pyrex tubing; an inner tube of 8 mm I.D. Pyrex tubing was attached to another Kontes valve, and both were tipped with inner 10/30 \$ ground glass joints.

Metal Vacuum Trap. A metal vacuum trap constructed of 1 5/8 in. O.D. copper tubing for the outer tube, and 5/8 in. copper tubing for the inner tube was used to trap substances which would otherwise attack glass. Two VWR brass valves were fitted to the trap as for the glass traps, but using Swagelok fittings.

Reaction Vessels. Depending upon the reaction conditions, vessels were composed of either Pyrex glass, fused silica, stainless steel, Monel, or Kel-F.

Pyrex glass round bottom flasks fitted either with ground-glass joints or with a Kontes high vacuum Teflon stopcock were used for reactions involving reagents or products which would not attack glass.

Hoke stainless steel vessels were used for reactions in which the pressure would not exceed 100 atm, and which did not involve the use of elemental fluorine. These vessels, which had a volume of 75 ml, were fitted with either Hoke or Whitey stainless steel valves to which brass 10/30 § inner joints were attached. For reactions requiring pressures up to 300 atm, a 100 ml Hoke Monel vessel equipped with a Whitey stainless steel valve was employed; a brass 10/30 § inner joint was fitted to the valve.

For reactions involving anhydrous hydrogen fluoride as the solvent system, 60 ml Kel-F cylindrical vessels with Teflon tops were employed. Whitey stainless steel valves were attached to the Teflon tops by Swagelok fittings.

Dry Box. All manipulations which required the use of an inert atmosphere were carried out in a Kewaunee Scientific Equipment dry box. Nitrogen was passed into the dry box through a tube filled with $CaSO_4$, and a large surface area of P_4O_{10} (used as a drying agent) was exposed to the atmosphere inside the dry box; an electric circulating fan inside the dry box facilitated the contact of the nitrogen atmosphere with the surface of the P_4O_{10}.

Physical Methods

Infrared Spectra. Infrared spectra over the range 4000 to $200cm^{-1}$ were recorded on a Perkin Elmer 467 spectrophotometer. Solid samples were run either neat between NaCl, KBr, or KRS-5 windows, or as KBr pellets. In general, the KRS-5 windows were most commonly used for neat solid smears as they are transparent down to $250cm^{-1}$ and are more chemically inert than KBr. Gaseous samples were recorded in a Monel gas cell fitted with either NaCl or KBr windows, and with a path length of 8.25 c.m.

Ultraviolet/Visible Spectra. Ultraviolet/visible spectra in the 700 to 200nm region were recorded on a Cary 14 spectrometer. Matched fused silica cells having a 1 cm pathlength were used for the sample and reference solutions. In all cases the reference solution was the same as the solvent used to make up the sample solution.

X-Ray Powder Spectra. X-Ray powder patterns were obtained with a General Electric XRD-5 camera using nickel filtered copper Kα radiation. Air sensitive samples were sealed under nitrogen in 0.5 mm quartz capillary tubes (Charles Supper Co., Inc.), while nonhydroscopic solids were sealed in the air. Exposure times were generally 4.0 ± 0.5 hr. Kodak No Screen X-Ray film was used to record line patterns, and the method was calibrated using known samples and comparing the calculated d-spacings with published ASTM values.

Melting Points. Melting points were determined using a Mel-Temp apparatus equipped with a mercury glass thermometer; the instrument had a range from ambient temperature to 400°C.

Elemental Analysis. Elemental analysis of new compounds was carried out by Beller Microanalytisches Laboratorium, Gottingen, West Germany. Air sensitive samples were sealed under vacuum in Pyrex glass tubes.

Molecular Weights. Molecular weights were determined by the vapor density method on the glass vacuum line. Pressures were measured by a mercury manometer using a cathetometer to achieve accurate readings. A 0.2096 liter Pyrex glass bulb fitted with a Fisher and Porter high vacuum stopcock was used for weight change measurements.

Gas Chromatography. Gas chromatographs were obtained on a Varian 3700 Gas Capillary Chromatograph. In addition to a strip chart recorder, the instrument was interfaced with a Varian CDS 111 Chromatography Data System which automatically integrated the sample peaks and retention times. The capillary column used was a 30 meter SE-54 with an O.D. of of 0.8 mm; a split ratio of 90 to 1 was needed for a typical sample injection of 0.6 ul. Column temperatures were adjusted to give the best possible separation within a 15 minute run time.

Reagents

Acetonitrile. Acetonitrile (CH_3CN) (Chrom AR) was obtained from Mallinkrodt Chemical Works and was used as received.

Allyl Alcohol. Allyl Alcohol ($CH_2 = CH\text{-}CH_2OH$) was obtained from Aldrich Chemical Co. and was used as received.

Antimony Pentafluoride. Antimony Pentafluoride (SbF_5) was obtained from Allied Chemicals; the volatile SbF_5 was vacuum transferred from the commercial container to a Pyrex glass vessel containing NaF, with subsequent evacuation at 0°C prior to its use.

Benzyl Alcohol. Benzyl Alcohol ($C_6H_5CH_2OH$) was obtained from Eastman Organic Chemicals and was used as received.

Chlorine Monofluoride. Chlorine Monofluoride (ClF) was obtained from Ozark-Mahoning and was used as received.

Chromium Trioxide. Chromium Trioxide (CrO_3) was obtained from Baker Chemicals. Prior to its use, CrO_3 was thoroughly dried under vacuum (10^{-3} torr) at 150°C for four hours. All subsequent manipulations using the dried CrO_3 were handled under an inert atmosphere.

Chromyl Chloride. Chromyl Chloride (CrO_2Cl_2) was obtained from Pflatz-Bauer Chemicals and Alfa Inorganics. The CrO_2Cl_2 was shaken in a vessel which contained mercury in order to remove Cl_2. The purified CrO_2Cl_2 was transferred in the vacuum line to the reaction vessel.

Chromyl Fluoride. Chromyl Fluoride (CrO_2F_2) was prepared by two methods developed by Green and Gard (27). The CrO_2F_2 from the reactor was transferred under vacuum to a stainless steel vessel containing dry KF. The purity of the CrO_2F_2 and the absence of HF or CrO_2ClF were confirmed by infrared analysis of the CrO_2F_2 in the gas phase. The spectrum was found to match that in the literature for pure CrO_2F_2 (37). Pure CrO_2F_2 was vacuum-transferred directly into the reaction vessel.

Cyclohexanol. Cyclohexanol ($C_6H_{12}O$) was obtained from Mallinkrodt Chemical Works and was used as received.

Dichloromethane. Dichloromethane (CH_2Cl_2) was obtained from Mallinkrodt Chemical Works and was fractionally distilled over $CaCl_2$ prior to use.

Fluorine. Fluorine (F_2), (98% purity), was obtained from Air Products. The fluorine was transferred directly from the tank, through a copper U-tube which contained nickel helicies and was cooled to -78°C to remove some of the HF. All operations involving the use of F_2 were carried out on a metal line as described in the "Physical Methods" section.

Heptanol. Heptanol ($C_6H_{14}O$) was obtained from Matheson Coleman and Bell and was fractionally distilled prior to use.

Hydrochloric Acid. Hydrochloric Acid (12 M "Baker Analyzed" Reagent) was obtained from Baker Chemical Company and was used as received.

Hydrogen Fluoride. Hydrogen Fluoride (HF) was obtained from Matheson and was used as received. All operations involving the use of HF were carried out on the metal vacuum line as described in the "Physical Methods" section, and all reactions employing HF as a solvent were carried out in Kel-F reactors.

Magnesium Fluoride. Magnesium Fluoride (MgF_2) was obtained from Alfa Inorganics, and was dried in a 120°C oven for a week before use.

Menthol. Menthol ($C_{10}H_{10}O$) was obtained from the Blumauer-Frank Drug Company; the infrared spectrum and the melting point matched those reported for pure menthol, and the solid was used as received.

Naphthyridine. Naphthyridine ($C_8H_6N_2$) was prepared according to literature methods (38) and its purity was established by melting point agreement with the reported value.

Nitryl Fluoride. Nitryl Fluoride (NO_2F) was obtained from Ozark-Mahoning. Prior to its use the commercially received lecture bottle was cooled to -78°C, and NO_2F was transferred into a metal vessel containing NaF; the NO_2F was then transferred from the metal vessel at -78°C into the reaction vessel via the metal vacuum line.

Oxygen. Oxygen (O_2) was obtained from Airco Inc. and was used as received.

Potassium Dichromate. Potassium Dichromate ($K_2Cr_2O_7$), (primary standard), was obtained from Mallinkrodt Chemical Works and was dried for several hours at 120°C before being used.

Potassium Fluoride. Potassium Fluoride (KF) was obtained from Baker Chemical Company as the anhydrous powder. Prior to its use the KF was heated at 120°C for several days.

N-Propanol. N-Propanol ($CH_3CH_2CH_2OH$) was obtained from Mallinkrodt Chemical Works. The propanol was fractionally distilled to remove impurities and the purity of the freshly distilled alcohol was confirmed by gas chromatographic analysis.

Pyrazine. Pyrazine ($C_4H_4N_2$) was obtained from the Aldrich Chemical Company, and was used as received.

Pyrazine-N-Oxide. Pyrazine-N-Oxide ($C_4H_4N_2O$) was prepared by the oxidation of pyrazine with 30% H_2O_2 in glacial acetic acid; the crude product containing acetate was dissolved in NaOH solution and crystallized out of this solution; mp 109-111°C.

Tripyridine. Tripyridine ($C_{15}H_{11}N_3$) was obtained from the G. Frederick Smith Chemical Company, and was used as received.

Xenon Difluoride. Xenon Difluoride (XeF_2) was obtained from PCR Research Chemicals, and was used as received.

CHAPTER III

CHEMISTRY OF CHROMIUM OXIDE FLUORIDES

Introduction

Oxychlorides of chromium have been known for at least 79 years; the most important of these is CrO_2Cl_2 which was synthesized as early as 1824 by Berzaelius (20). In general, the chemistry of the oxide chlorides has preceded that of the oxide fluorides, though neutral oxyfluorides of chromium in oxidation states from +3 to +5 are now known.

CrOF has been reported, but not isolated, in the reaction of CrF_3 and Cr_2O_3 in KF (39a), and as a by-product in the fluorination of chlorinated hydrocarbons in aqueous HF in the presence of a Cr-Al catalyst at 275-425°C (39b).

$CrOF_2$ has been reported by Rochat et al. (40); it is formed as an inert brown-black solid by the thermal decomposition of CrO_2F_2.

III-1 $CrO_2F_2 \xrightarrow{500°C} CrOF_2 + 1/2\ O_2$

$CrOF_2$ is stable under vacuum even at 1600°C.

As with the trivalent and tetravalent chromium oxyfluorides, only one neutral compound, $CrOF_3$, exists for the pentavalent state; its preparation and chemistry are the focus of this chapter, and will be discussed in detail.

Two oxyfluorides of hexavalent chromium are known, CrO_2F_2 and $CrOF_4$. First reported as a by-product in the reaction of F_2 with Cr metal in a glass flow system, $CrOF_4$ was separated from other reaction products by careful fractional distillation as a dark red solid which melted at 55°C without decomposition (13b). $CrOF_4$ has also been formed by the fluorination of CrO_3 at 220°C; interestingly, at 150°C, CrO_2F_2 was the major product, while at 250°C, CrF_5 was the major product (13b). Although Edwards and co-workers were successful in isolating $CrOF_4$ and studying some of its physical properties, attempts to reproduce their work were largely unsuccessful (19).

In contrast to $CrOF_4$, CrO_2F_2 is easily prepared, and its chemistry is much better understood. First prepared by Engelbrecht and Grosse (41), CrO_2F_2 is a volatile dark violet-red solid which melts at 31.6°C, and is thermally stable in the absence of light at temperatures below 500°C. Many preparative routes to CrO_2F_2 are known (26), and its chemistry with inorganic systems has been investigated. For example, CrO_2F_2 reacts with alkali and alkaline metal fluorides to form fluorochromate salts (42):

III-2 $2MF + CrO_2F_2 \longrightarrow M_2CrO_2F_4$
$M = Na, K, Cs$

III-3 $MF_2 + CrO_2F_2 \longrightarrow MCrO_2F_4$
$M = Mg, Ca$

Reactions with Lewis acids produce chromyl compounds,

III-4 $CrO_2F_2 + 2SO_3 \xrightarrow{25°C} CrO_2(SO_3F)_2$

III-5 $CrO_2F_2 + TaF_5 \xrightarrow{60°C} CrO_2F(TaF_6)$

III-6 $CrO_2F_2 + SbF_5 \xrightarrow{25°C} CrO_2F(SbF_6)$

III-7 $CrO_2F_2 + 2SbF_5 \longrightarrow CrO_2(Sb_2F_{11})$

and with Lewis bases (43)

III-8 $CrO_2F_2 + NO_2F \longrightarrow NO_2CrO_2F_3$

III-9 $CrO_2F_2 + NOF \longrightarrow NOCrO_2F_3$

Impure chromium oxide trifluoride ($CrOF_3$) was first prepared by Sharpe and Woolf by the reaction of CrO_3 with BrF_3 (6). It was found, however, that the resulting $CrOF_3$ product could not be completely freed of BrF_3 even after heating to 200°C under vacuum. Other attempts by Clark and Sadana to prepare pure $CrOF_3$ by the reactions of CrF_4 and CrO_3 with various interhalogen agents also resulted in impure products (7, 17):

III-10 $CrF_4 + BrF_3 \xrightarrow{reflux} CrOF_3 \cdot 0.25BrF_3$

III-11 $CrO_3 + BrF_3 \xrightarrow{25°C} CrOF_3 \cdot 0.25BrF_3$

III-12 $CrO_3 + BrF_5 \xrightarrow{25°C} CrOF_3 \cdot 0.25BrF_5$

III-13 $CrO_3 + ClF_3 \xrightarrow{12°C} CrOF_3 \cdot 0.25ClF$

The use of quartz reaction vessels presumably provided the oxygen in III-10. All attempts to purify the products by heating under vacuum resulted in decomposition. The impure products were dull red, fumed when exposed to air, and had magnetic moments consistent with chromium(V).

In an attempt to prepare CrO_2F_2 by the action of ClF on CrO_3, Green found that a large excess of ClF, or reaction temperatures above 0°C, led to diminished amounts of CrO_2F_2

and the formation of an unstable red brick colored solid (44), the solid hydrolyzed to a yellow-green solution in H_2O, and had a magnetic moment consistent with a d^1 Cr(V) compound. Elemental analysis of this solid indicated an impure product of composition $CrOF_3 \cdot 0 \cdot 14ClF$ to $CrOF_3 \cdot 0.21ClF$. It was thought that further fluorination of the impure $CrOF_3$ might result in the formation of $CrOF_4$. What was observed, however, was that the reaction of F_2 with the impure $CrOF_3$ at 120°C produced a non-volatile purple solid with a greatly reduced chlorine content.

In an extension of this work, Johnson was able to prepare good quality $CrOF_3$ by the following reaction (19):

III-14 $CrO_3 + (4\ \text{to}\ 5)\ ClF \xrightarrow[4\ hr]{110°C} CrOF_3 \cdot xClF$

$3/2Cl_2 + yClO_2F.$

Heating the crude $CrOF_3$ product three times with fluorine at 120°C for 12, 2, and 3 hr, with the vessel being evacuated and repressurized with fresh fluorine at each treatment stage, pure $CrOF_3$ was obtained as a nonvolatile purple solid, as in equation 15.

III-15 $CrOF_3 \cdot xClF + F_2 \longrightarrow CrOF_3 + ClO_2F$

Because ClO_2F was the only identified volatile chlorine containing material found from the F_2 treatments, it seems likely that the contaminating species is not unreacted ClF. Based on infrared evidence, Green suggested that the actual contaminant is the $ClO_2^+CrOF_4^-$ ion pair (44). The resulting solid obtained after the high temperature fluorine treatments was a bright purple compound; the elemental analysis of the solid agreed very closely with the theoretical values expected for $CrOF_3$. However, in some samples, a small amount of residual chlorine containing species remained associated with the $CrOF_3$ (0.49% by weight).

The purple $CrOF_3$ was found to be mildly hygroscopic, hydrolyzed to a yellow-green solution in H_2O, and attacked glass at 300°C which was accompanied by apparent melting. When heated to 300°C for five hours, $CrOF_3$ decomposed to CrF_3 and O_2 (19).

The author found that attempts at preparing $CrOF_3$ by this method, including using oxygen as well as fluorine to remove ClO_2F, often result in a rose colored solid which slowly decomposes in the dry box atmosphere, making the $CrOF_3$ somewhat difficult to handle. An infrared spectrum of the rose colored $CrOF_3$ looks identical to that reported for purple $CrOF_3$ (36). It is likely that the rose colored $CrOF_3$ is less stable than the purple $CrOF_3$ due to greater chlorine containing contaminant.

In an effort to prepare $CrOF_4$ by the reaction of CrO_2F_2 and XeF_2, Johnson (45) found that at 260°C the reaction produced $CrOF_3$. In an extension of this work, highly pure $CrOF_3$ has been prepared. The possibility of any chlorine containing contaminant is precluded by this synthetic route, and the deep blueish-purple solid formed in this manner appears unchanged even when exposed to moist air for several minutes. The infrared spectrum of this highly pure $CrOF_3$ is identical to that found for the previously reported $CrOF_3$ (18), with the exception of the intensities of two of the bands (380 and 359cm^{-1}), both of which appear as very weak absorptions for this $CrOF_3$.

In order to further elucidate the chemistry of chromium oxide trifluoride, $CrOF_3$ (prepared by the ClF method) was reacted with group IA and IIA metal fluorides and SbF_5 in anhydrous hydrofluoric acid. Although the reactions with the metal fluorides produced solids for which unique x-ray patterns and infrared spectra were obtained, it proved very difficult to drive off all of the HF from these products. Consequently, the elemental analyses for these products, with the exception of K_2CrOF_5, were not close to the calculated values expected for simple $MCrOF_4$ and $MCrOF_5$ salts of Na, K, and Mg. The discrepancies in the elemental analyses may also have been caused by incomplete reactions complicated by impurities in the reactants, or in the hydrogen fluoride. The reaction with SbF_5 produced a purple solid which fumed in the dry box atmosphere, presumably due to residual SbF_5; efforts to remove the SbF_5 by heating under vacuum resulted in the loss of oxygen and the formation of $CrF_2Sb_2F_{11}$.

Reaction of XeF_2 with MO_2F_2 (M = Mo, W) in hydrofluoric acid has been found to yield MOF_4 (46). An attempt to synthesize $CrOF_4$ by this method failed, yielding instead a blood red solid which as yet remains unidentified.

Experimental

Reaction of CrO_3 and ClF With Subsequent Fluorine Treatments. 2.0g (20 mmol) CrO_3 was added to a well passivated 100 ml Monel vessel and heated at 140° to 160°C for 4 hr under vacuum. After cooling the vessel to -196°C, 3.5g (100 mmol) ClF were condensed into the vessel. The reaction was then heated to 110°C for 5 hr. After removal of all room temperature volatile materials, the vessel was pressurized with 2 to 3 atm F_2, and heated for 4 hr at 110° to 120°C; this treatment was carried out four times, with excess F_2 being vented out at -196°C, and room temperature volatile materials pumped away between each fluorine treatment. The $CrOF_3$ prepared in this manner was a deep rose-purple color which gave an infrared spectrum identical to the reported spectrum (18).

Reaction of CrO_3 and ClF With Subsequent Fluorine and Oxygen Treatments. 4.97g (49.7 mmol) dried CrO_3 was loaded into a 100 ml Monel vessel; to this, 10.93g (200.7 mmol) ClF was added. The reaction was then heated to 118°C for 6 hr with periodic shaking after which the vessel was cooled to -196°C and volatile materials removed. The volatile material showed no infrared absorptions and did not attack mercury; these observations indicate that the material was

O_2. The vessel was placed back in the furnace at 118°C for 5 hr. Upon cooling to -196°C, the only volatile material found was O_2 (molecular weight found, 30.2 g/mole; requires 32.0g/mole). The volatile material again showed no infrared active vibrations and did not attack mercury. The volatile materials at -127°C attacked mercury as well as the NaCl windows of the infrared gas cell. Consequently, the molecular weight determination of 147g/mole was likely inaccurate. The infrared spectrum showed an absorption attributable to SiF_4, and two unidentified peaks at 946cm^{-1} and 1285cm^{-1}. Only a slight amount of volatile materials were present at room temperature. 1 atm O_2 was added to the vessel, and the reactants were heated for 5.3 hr at 120°C. Excess O_2 was removed at -196°C. At -127°C a volatile material which attacked mercury was released; the molecular weight was measured to be 140.4g/mole, and the infrared spectrum showed only a peak due to SiF_4. Volatile materials at room temperature were shown to be ClO_2F, CrO_2F_2, and HF by characteristic infrared absorptions.

The vessel was again charged with 1 atm O_2 and heated to 120°C for 3.7 hr. Volatile materials at -196°C were pumped away, and the reaction was warmed to room temperature. The -196°C trap contents of the room temperature volatile materials were deep reddish-brown solids which became a reddish-yellow gas upon warming. The infrared spectrum of these volatile materials showed a characteristic absorption for SiF_4, and an unidentified band (broad and split) centered at $1098cm^{-1}$.

The vessel was then charged with 5.5 mmol F_2 and heated at 120°C for 6 hr. Excess F_2 was vented at -196°C and the vessel was evacuated at that temperature through a $CaCl_2$ tube. Upon warming the vessel to room temperature, a yellow solid formed in the -196°C trap; an infrared spectrum of the trap contents showed characteristic absorptions for ClO_2F and SiF_4, along with unidentified bands at $946cm^{-1}$ and $1098cm^{-1}$.

The vessel was again pressurized with 5.5 mmol F_2 and heated to 120°C for 6 hr. The reaction was cooled to -196°C and F_2 was removed as above. The room temperature volatile materials were again trapped at -196°C and analyzed; the infrared spectrum of the volatile materials showed an absorption due to SiF_4, and unidentified absorptions at $946cm^{-1}$ and $1098cm^{-1}$.

The reaction was treated once more with F_2 (7 hr, 120°C), evacuated, and heated for 16 hr at 120°C with 1 atm O_2. The volatile materials (other than O_2) showed only a slight absorption at 1098 cm^{-1} in the infrared spectrum.

Following thorough evacuation, the vessel weight corresponded to 6.98g $CrOF_3$; the theoretical weight of $CrOF_3$ should be 6.21g. Upon opening the vessel in the dry box, a purple solid remained. The infrared spectrum of this solid taken neat between KRS-5 windows was identical to that reported for $CrOF_3$ (16).

Reaction of CrO_2F_2 and XeF_2. 0.7190g (4.25 mmol) XeF_2 was loaded into a well passivated 75 ml stainless steel vessel. The vessel was cooled to -196°C, evacuated, and 1.38g (11.3 mmol) CrO_2F_2 were transferred in on the vacuum line. The reaction was then placed in a 230°C furnace and heated slowly to 270°C over a 4.4 hr period. Upon opening the vessel at -196°C on the vacuum line through a trap cooled to 196°C, volatile materials were released; the volatile material was identified as O_2 by a molecular weight determination: found 32.9g/mole requires 32.0 g/mole. The weight loss of volatiles corresponded to 0.07g (2.19 mmol) O_2, (theor. 0.13g (4.25 mmol)). The reaction was placed back in the furnace at 240°C and heated to 278°C over a 2.5 hr period; the vessel was shaken periodically during this time. The vessel was then cooled to -196°C as above and 1.23 cm volatile materials were released, and identified as O_2. The weight loss of 0.03g (0.94 mmol) O_2 brought the total loss of O_2 to 0.10g (3.13 mmol). The reaction was then further heated to 275°C for 3.8 hr with periodic shaking. Upon cooling the reaction to -196°C and removing volatiles as above, the change in weight corresponded to 0.02g (0.63 mmol) O_2, bringing the total weight loss to 0.12g (3.75 mmol) O_2.

The reaction was then cooled to -98°C and connected to the vacuum line through two traps in series; the trap nearest the vessel was cooled to -98°C while the second trap was cooled to -196°C. Upon opening the reaction vessel, a white condensate formed in the -98°C trap, and the Xe condensed in the -196°C trap; the Xe was revolatilized and identified by its molecular weight: found, 130.9 g/mole; requires, 131.3 g/mole. The white condensate in the -98°C trap could not be revaporized. The weight loss of the vessel after complete removal of the -98°C volatile materials corresponded to 0.53g (4.05 mmol) Xe.

Since it appeared, from the weight loss of O_2 and Xe, that the reaction was not yet complete, the reaction was heated further to 270°C over a 2 hr period. Upon cooling to -196°C and checking for volatile materials as above, less than 1 mm were observed, and the weight change of the vessel was 0.01g, insignificant within experimental error. The reaction was then warmed until just hot to the touch and evacuated through a trap cooled to -196°C; only SiF_4 and unreacted CrO_2F_2 could be identified in the infrared spectrum of the trap contents. The final vessel weight corresponded to 0.94g of product.

The vessel was opened under nitrogen in the dry box; small shiney deep purple crystals were formed at the neck of the vessel and coating the bottom of the valve, while the inner vessel walls were coated with a powdered form of the solid. An infrared spectrum (Figure 4) was identical to

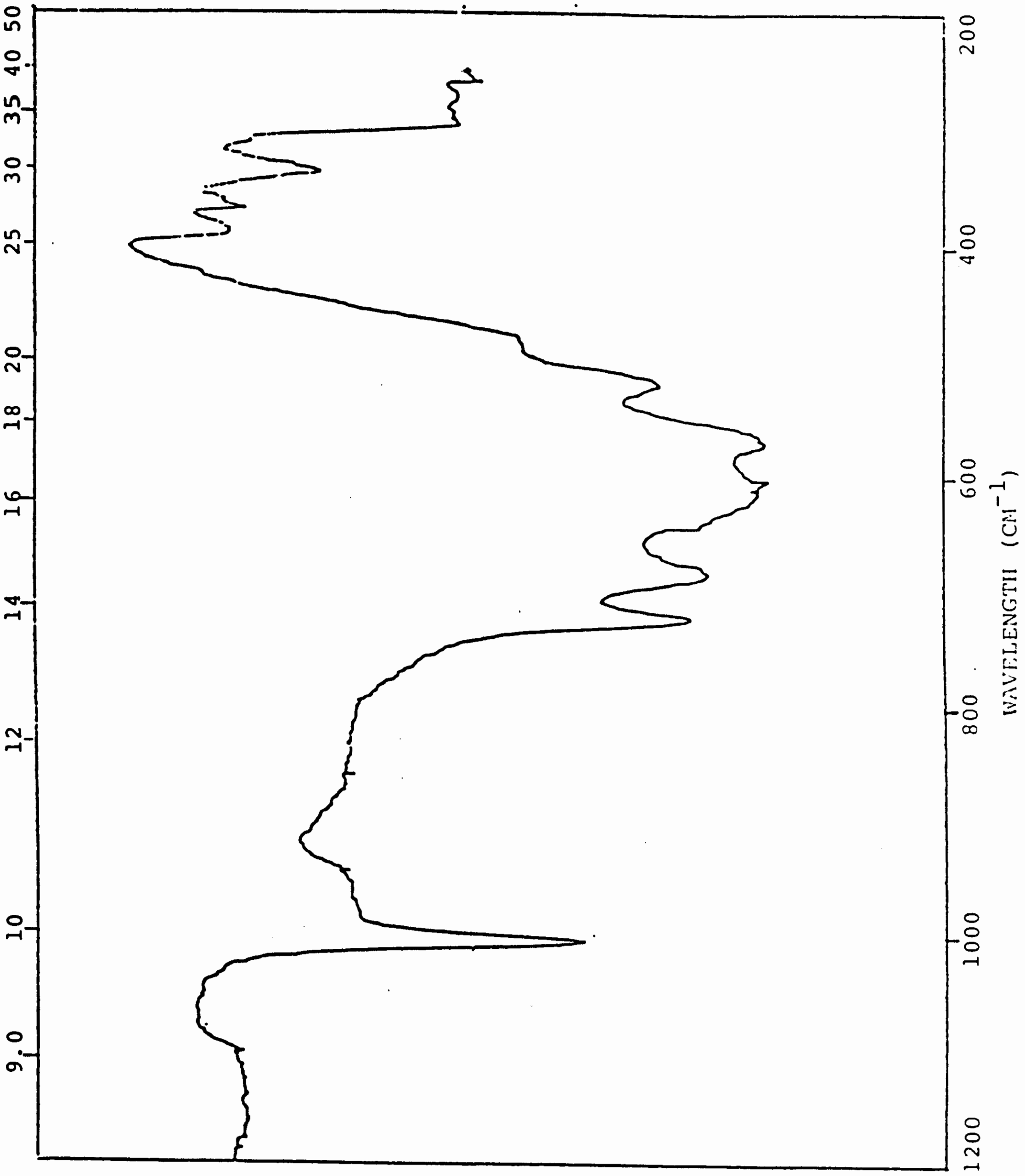


FIGURE 4. Infrared spectrum of $CrOF_3$ prepared by the reaction of CrO_2F_2 with XeF_2

that reported for $CrOF_3$ (18). The x-ray powder pattern of this $CrOF_3$ is shown in Table I. Yield, 7.52 mmol (94%) $CrOF_3$.

Reaction of $CrOF_3$ With NaF in Anhydrous HF. 1.4509g (11.6 mmol) $CrOF_3$ (prepared by the ClF method) was loaded into a Kel-F reaction vessel equipped with a Teflon coated magnetic stir bar. 0.9747g (23.21 mmol) NaF was then loaded into the vessel and 15 ml HF was condensed into the vessel via the metal line. Upon warming, the solution became dark green, but the $CrOF_3$ remained largely undissolved. The solution was stirred at room temperature for 19.5 hr during which time an off-white solid formed. The HF was then removed at room temperature and the vessel was opened in the dry box. An infrared spectrum showed excess HF (as the HF_2^- anion) remaining in the solid, and a melting point measurement showed no melting up to 250°C.

The vessel was resealed and heated to 100°C under vacuum through a trap cooled to -196°C in an attempt to remove the excess HF. After 3 hr of heating, the solid became a pale yellow color; an infrared spectrum of this solid showed that HF still remained in the solid. An infrared spectrum of the -196°C trap contents showed only SiF_4. The vessel was resealed and the reaction was further heated for 4 hr at temperatures up to 130°C under vacuum. An infrared spectrum of this newly heated solid showed that HF still remained in the solid. In a sealed capillary tube,

TABLE I

X-RAY POWDER PATTERN OF $CrOF_3$ PREPARED BY THE REACTION OF XeF_2 + CrO_2F_2

d(A)	Intensity	d(A)	Intensity
5.79	mw	1.817	s
4.91	s		
4.44	s	1.774	m
4.18	s	1.685	ms
3.99	mw	1.597	vs
3.74	ms	1.551	w
3.63	ms	1.524	m
3.35	vs	1.482	ms
2.82	mw	1.457	w
2.74	mw	1.423	ms
2.56	m	1.407	ms
2.48	ms	1.368	w
2.35	mw	1.363	w
2.23	s	1.330	m
2.040	ms	1.310	w
2.013	m	1.285	mw
1.943	m	1.277	w
1.892	mw	1.233	s
1.865	w	1.199	s

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak the pale yellow solid remained unchanged up to 200°C, turned orange above 200°C, but failed to melt up to 350°C. Yield, 2.1g.

The x-ray powder pattern of this solid showed no unreacted $CrOF_3$ or NaF (Table II), and the infrared spectrum showed strong absorptions attributable to ν Cr=0 and ν Cr-F, a medium weak absorption which may be attributable to a Cr-0-Cr vibration, and a weak absorption due to HF_2^- (Figure 5). Analysis calculated for Na_2CrOF_5: Cr, 24.8; F, 45.5. Found Cr, 21.4; F, 39.5; H, 0.11.

Reaction of $CrOF_3$ With KF in Anhydrous HF. 0.8859g (7.1 mmol) $CrOF_3$ (prepared by the ClF method) was loaded into a Kel-F reaction vessel equipped with a Teflon coated magnetic stir bar. 0.7861g (13.5 mmol) KF was added, and 15-20 ml HF was condensed into the vessel through a copper U-tube (previously passivated with HF) on the metal line. The reaction was warmed to room temperature and stirred for 12 hr; the resulting dull green solution contained no undissolved solid. The HF was then removed and the vessel was further evacuated at room temperature for 12 hr; the final weight of the vessel corresponded to an excess of 0.4g (20 mmol) HF. The reaction was then heated under vacuum between 50°C and 75°C for 7.3 hr, resulting in a loss of 0.3g (15 mmol) HF; further heating under vacuum resulted in no further weight loss. The final vessel weight corresponded to 0.1g (5 mmol) excess HF. Yield, 1.8g

TABLE II

X-RAY POWDER PATTERN OF Na_2CrOF_5 (impure product)

d(A)	Intensity	d(A)	Intensity
5.98	w	2.14	m
5.45	m	2.067	vw
4.95	m	1.991	w
4.47	vs	1.930	s
3.84	mw	1.873	w
3.46	s	1.818	mw
3.16	s	1.770	vw
2.67	vw	1.721	mw
2.58	w	1.684	w
2.37	vw	1.644	mw
3.32	w	1.485	m

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

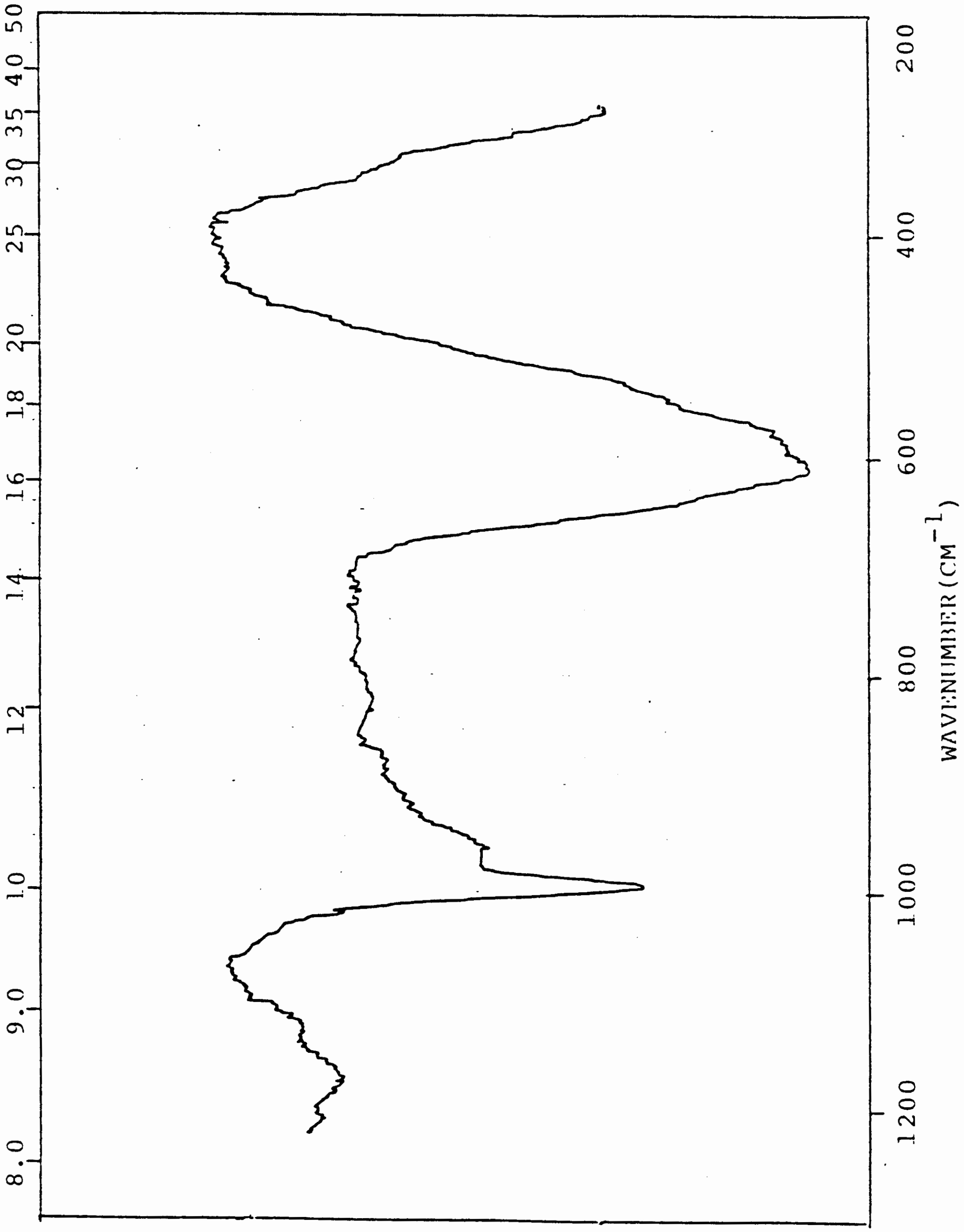


FIGURE 5. Infrared Spectrum of Impure Na_2CrOF_5.

(theor. 1.7g).

Upon opening the vessel in the dry box, the vessel contained a yellow powdery solid. An infrared spectrum showed absorptions attributable to ν Cr=O, ν Cr-F, and HF_2^- (Figure 6). The x-ray powder pattern was unique, and showed no lines attributable to unreacted $CrOF_3$ or KF (Table III). A melting point determination in a sealed capillary tube showed that the solid remained yellow up to 128°C, but decomposed immediately at that temperature accompanied by vigorous glass attack. Interestingly, a sample heated under vacuum to 170°C remained yellow without melting; an infrared spectrum of this material was essentially identical to that found for the HF_2^- contaminated material. A sample of the solid heated to 170°C was used for an elemental analysis. Analysis calculated for K_2CrOF_5: F, 39.4; Cr, 21.6. Found: F, 40.8; Cr, 19.6; C, 0.18; H, 0.49.

Reaction of $CrOF_3$ and MgF_2 (1:1) in Anhydrous HF. 1.4549g (11.64 mmol) $CrOF_3$ (prepared by the ClF method) was loaded into a Kel-F vessel equipped with a Teflon coated magnetic stir bar. 0.7249g (11.64 mmol) MgF_2 was added, and HF was condensed into the vessel through a well passivated (with HF) copper transfer tube on the metal line. The reaction was stirred for four days, during which an insoluble off-white solid formed. Upon cooling the reaction to -196°C, 1.3mm of noncondensible material was found; presumably this was O_2 as no mercury attack was observed. The HF

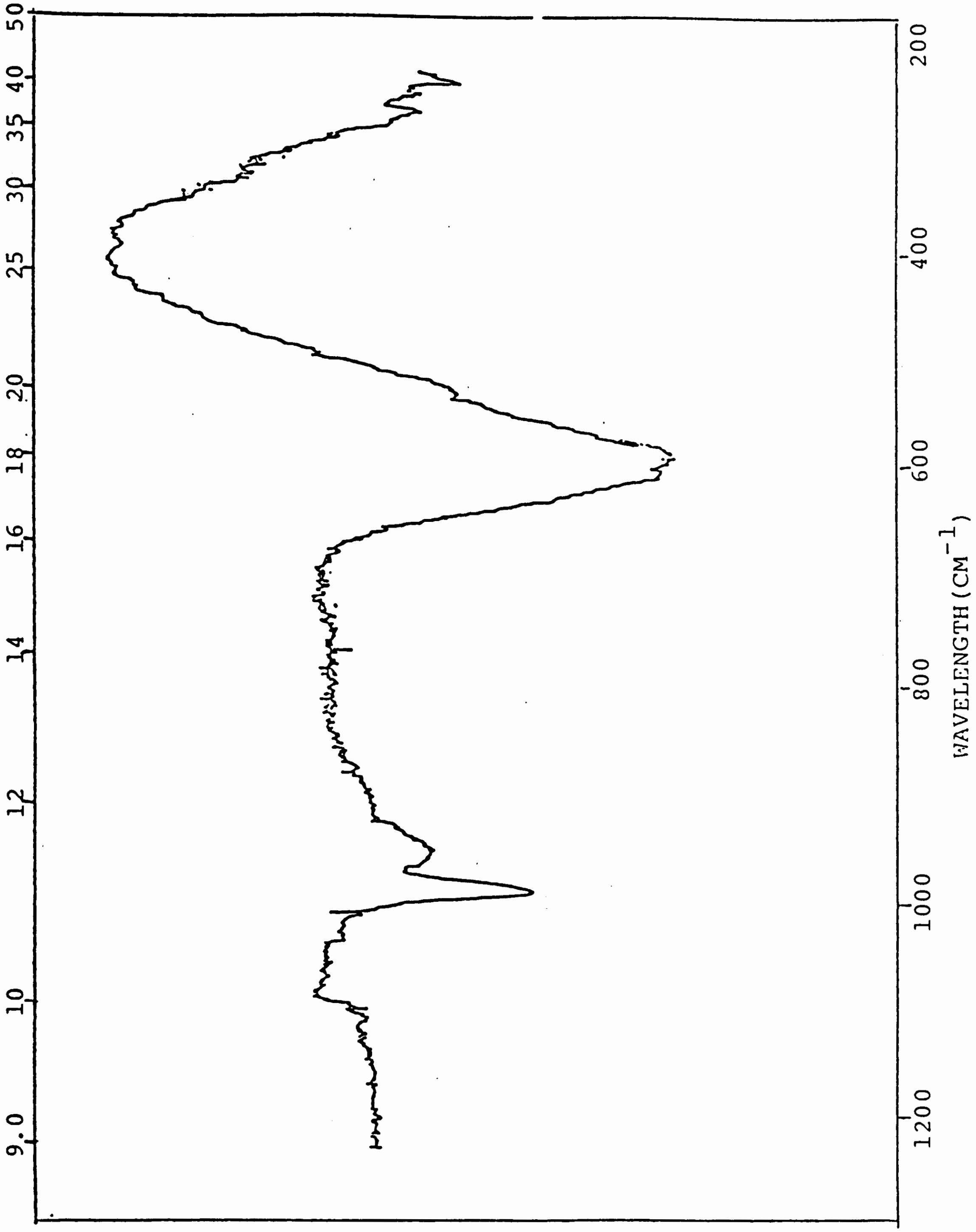


FIGURE 6. Infrared spectrum of K_2CrOF_5

TABLE III

X-RAY POWDER PATTERN OF K_2CrOF_5

d(A)	Intensity	d(A)	Intensity
5.07	m	1.976	ms
4.49	s	1.928	vw
3.97	s	1.774	w
3.36	vw	1.627	m
3.14	m, br	1.597	m
2.82	s	1.529	vw
2.64	w	1.491	vw
2.42	w	1.401	w
2.37	ms	1.333	w
2.19	w	1.251	w
2.15	vw		

s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, br = broad was then removed and the vessel was further evacuated for 4 hr at room temperature. The final weight corresponded to 2.05g of product (theor. $MgF_2 + CrOF_3 = 2.18g$). The vessel was opened in the dry box revealing a chalk white powdery solid.

The infrared spectrum of this solid is shown in Figure 7, and the x-ray powder pattern is shown in Table IV. The solid appeared to melt at 272°C accompanied by extensive glass attack. An iodimetric tritration for Cr(VI) (based on $3Cr(V) \longrightarrow 2\ Cr(VI) + Cr(III)$) resulted in a value of 21.8% total Cr (theor. 27.8%).

Reaction With $CrOF_3$ and MgF_2 (1:0.5 in Anhydrous HF. 0.4966g (3.97 mmol) $CrOF_3$ (prepared by the ClF method) was loaded into a Kel-F reaction vessel equipped with a Teflon coated magnetic stir bar. 0.1319g (2.12 mmol) MgF_2 (thoroughly dried by heating to 110°C under vacuum for 21 hr) was added, and HF was condensed into the vessel through a well passivated (HF) copper transfer tube on the metal line. The reaction was stirred at room temperature for 19 hr, during which an off-white solid formed and the HF solution became a brownish color. The HF was then decanted from the solid under a stream of nitrogen, and fresh HF was condensed into the vessel as above. The solid was stirred in the fresh HF; the resulting golden amber colored HF was again decanted, and fresh HF was again condensed into the vessel. After decanting the HF out of the vessel, the

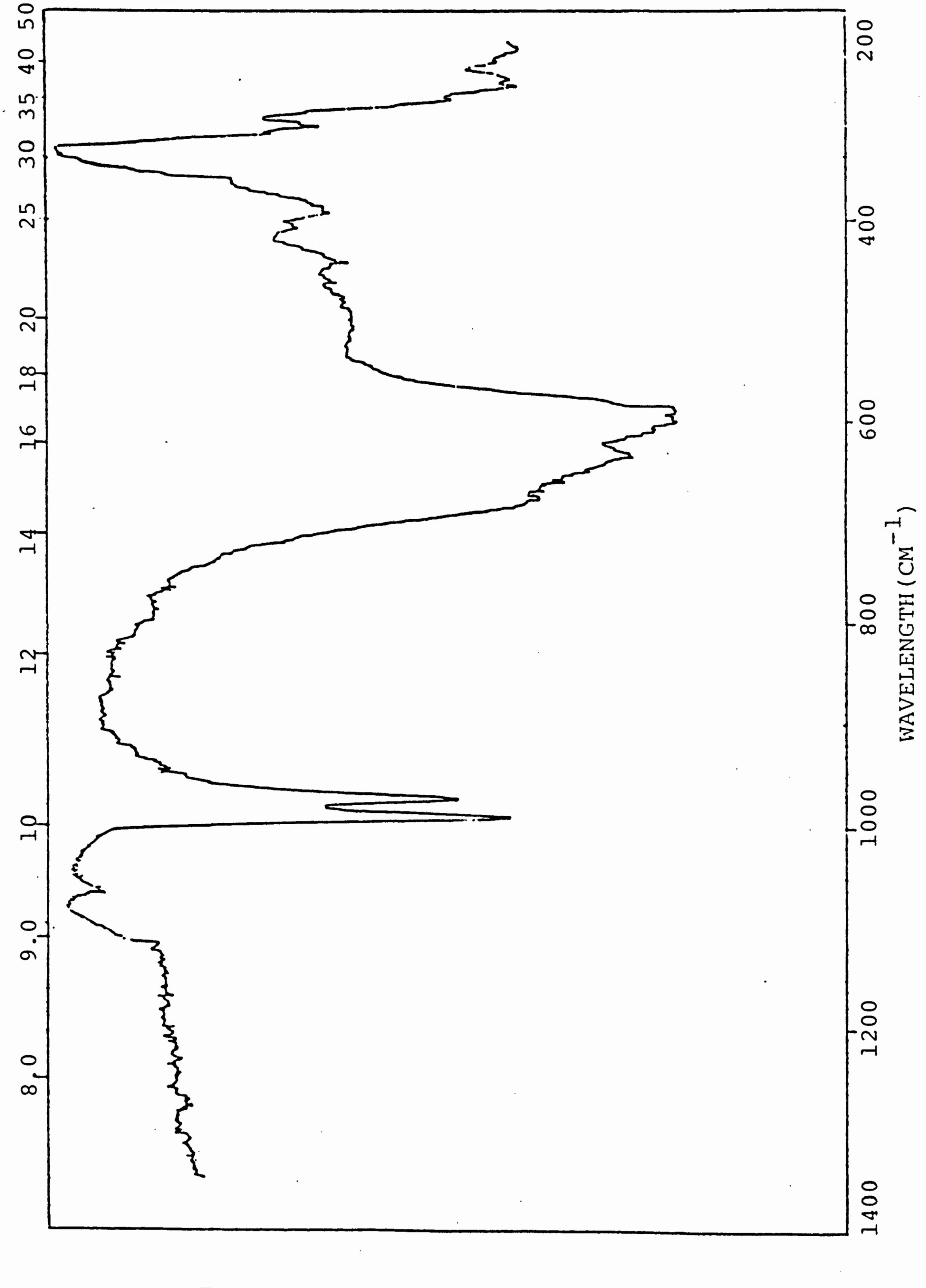


FIGURE 7. Infrared spectrum of impure $MgCrOF_5$

TABLE IV

X-RAY POWDER PATTERN OF $MgCrOF_5$ (impure product)

d(A)	Intensity	d(A)	Intensity
9.44	mw	2.16	vw
8.50	s	2.13	vw
7.65	s	2.058	m
6.34	ms	2.047	s
6.08	w	1.979	w
5.27	m	1.936	vvw
5.06	m	1.906	mw
4.77	w	1.864	w
4.52	s	1.832	m, br
4.29	ms	1.785	mw, br
4.07	s, br	1.742	mw, br
3.79	s	1.715	m, br
3.66	vs	1.628	m, br
3.40	s	1.604	vw
3.28	ms	1.581	w
3.16	ms	1.557	mw
2.96	w	1.531	mw
2.89	ms	1.508	w
2.65	vw	1.469	vw
2.57	vvw	1.444	mw
2.51	m, br	1.408	vw
2.47	m, br	1.379	mw
2.40	mw	1.360	w
2.36	vw	1.331	w, br
2.30	vvw	1.293	vw
2.23	s, br	1.287	vw

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, br = broad

residual HF was removed under vacuum and the solid became a light tan color. The vessel weight after removal of HF corresponded to 0.24g of product (theor. 0.63g), indicating that the product was slightly soluble in HF. The vessel was further evacuated for 8 hr at room temperature, and for 6 hr at 60-70°C. The vessel was opened in the dry box and 0.13g of the off-white solid was placed in a clean Kel-F vessel and heated to 104°C for 2 hr through a trap cooled to -196°C. This heating resulted in a weight loss of 0.08g. An infrared spectrum of the trap contents showed absorptions in the regions characteristic for ν C=C and ν C-Cl. An infrared spectrum of the solid showed a well resolved ν Cr=0 region, but a poorly resolved ν Cr-F region (Figure 8).

Continued heating of the solid at 100°C for 6 hr, 120°C for 5 hr, up to 150°C over 4 hr, and at 150°C for 2.5 hr resulted in the solid becoming a pale yellow color. An infrared spectrum of this solid (neat, AgCl windows) was identical in the ν Cr=0 region to that obtained previously, but the ν Cr-F region was better resolved (Figure 9). The latter spectrum showed no absorptions characteristic of the HF_2^- anion.

The melting point measurements were quite similar for the pale yellow and off-white solids; both became discolored at 160°C to 180°C, turned dark brown at 240°C, and did not melt up to 400°C. Neither solid could be successfully packed into x-ray capillary tubes. Analysis calculated for

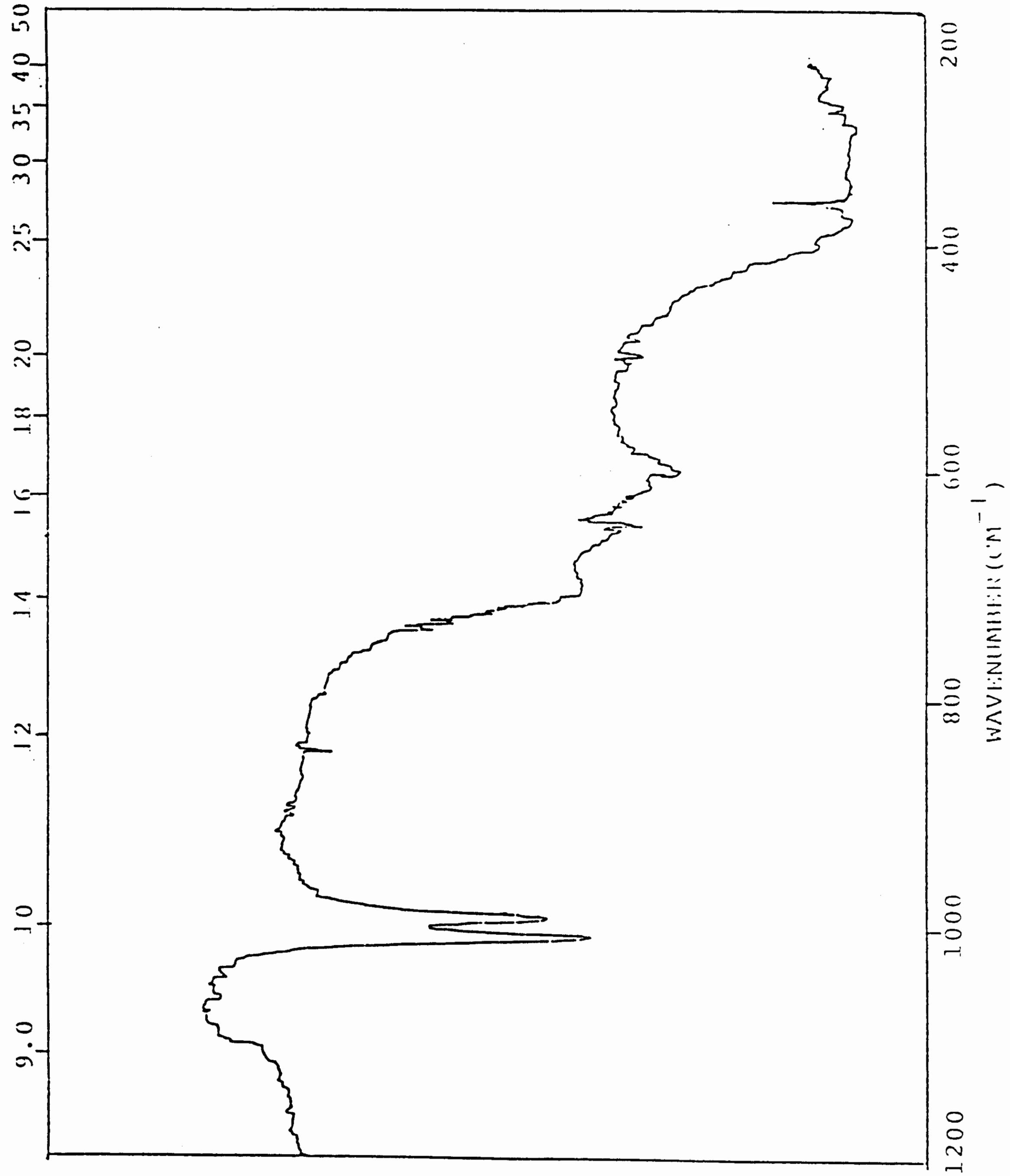


FIGURE 8. Infrared spectrum of impure $Mg(CrOF_4)_2 \cdot 2HF$

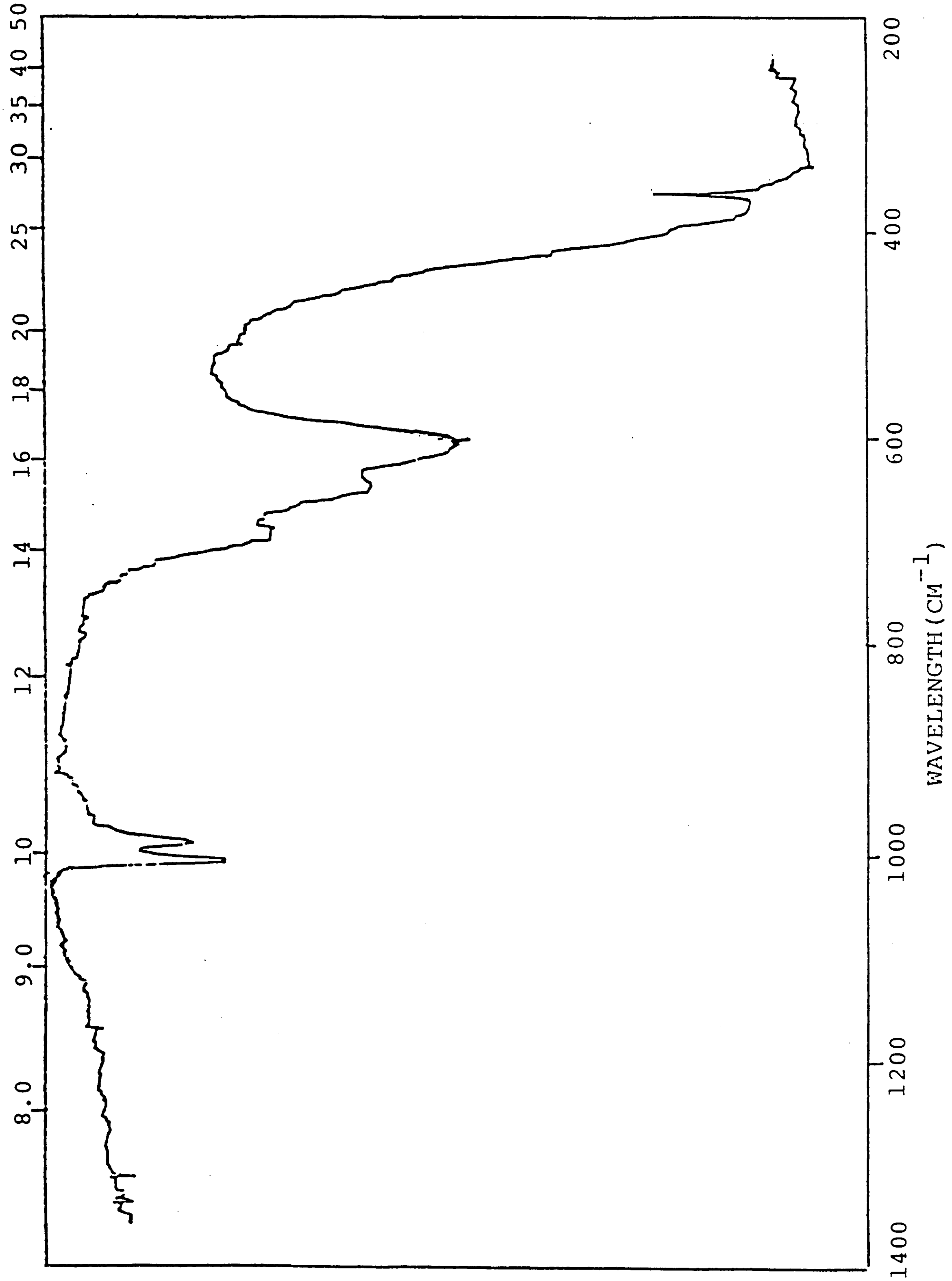


FIGURE 9. Infrared spectrum of impure Mg(CrOF$_4$)$_2^-$

off-white $MgCr_2O_2F_8 \cdot 2HF$: H, 0.58; Cr, 30.4; F, 55.50. Found: H, 0.54; Cr, 26.4; F, 36.1; C, 0.58. Analysis calcualted for pale yellow $MgCr_2O_2F_8$: Cr, 33.3; F, 48.7. Found: Cr, 26.6; F, 29.6.

Reaction of $CrOF_3$ With SbF_5 in Anhydrous HF. 2.62g (12.4 mmol) SbF_5 was transferred from a quartz vessel containing KF into a Kel-F vessel equipped with a Teflon coated magnetic stir bar. After evacuation at 0°C, the vessel was opened in the dry box and 0.6490g (5.2 mmol) $CrOF_3$ (prepared by the ClF method) was added. The vessel was then cooled to -196°C, evacuated, and HF condensed in through a well passivated copper transfer tube on the metal line.

After stirring the solution for 40 min at room temperature, the solution became a purple color, though much of the $CrOF_3$ remained undissolved. After stirring for 7 days at room temperature, the HF solution became a rose purple color, and a light purple solid was evident; the solid did not appear to be $CrOF_3$. The reaction was stirred for 9 more days at room temperature, after which time the reaction appeared unchanged. After further stirring the reaction for 13 days at room temperature, the reaction was cooled to -196°C; 1.8mm of volatile material was observed (likely O_2 since no mercury attack was observed). The HF was transferred out, and the vessel was evacuated at room temperature for 2 hr, and further evacuated at 30°C for 13 hr until constant weight was achieved. The final weight corresponded to 3.04g product (theor. 3.15g for $CrOF_3 \cdot 2SbF_5$).

Upon opening the vessel in the dry box, cloudy fumes filled the vessel above a light purple sticky solid. A melting point measurement showed that the solid was stable up to 50°C. The vessel was resealed, and further evacuated at 30°C to 40°C for 6 hr through a trap cooled to -196°C. An infrared spectrum of the trap contents showed only a weak absorption at 1000 cm^{-1}. The vessel was again opened in the dry box; the white cloudy fumes persisted, as did the sticky purple solid. The vessel was closed, and the reaction was further heated under vacuum, this time to 60°C. The solid in contact with the vessel walls became slightly brown. Upon opening the vessel in the dry box the white cloudy fumes remained, but the solid seemed much less sticky. The solid melted with decomposition at 220°C. An infrared spectrum of the purple solid (neat, KRS-5 windows) showed absorptions characteristic of νCr-F, but none in the νCr=O region.

Reaction of XeF_2 and CrO_2F_2 in Anhydrous HF. 0.14g (0.827 mmol) XeF_2 was loaded into a Kel-F vessel equipped with a magnetic stir bar. The vessel was cooled to -196°C, evacuated, and 6.6 ml of HF was condensed into the vessel through a well passivated (HF) copper transfer tube on the metal line. 0.24g (2.38 mmol) CrO_2F_2 was then transferred into the vessel, and the reaction was allowed to warm slowly to room temperature. The reaction was stirred for 27 min at room temperature, and then cooled to 0°C and stirred for 20 hr. The reaction was then cooled to -196°C and checked for volatile materials; none were found. The vessel was then warmed to -97.8°C and again checked for volatile materials; 2.58 cm were found (mol. wt. 165 g/mole). An infrared spectrum of the volatile material showed no absorptions; the volatile material was likely Xe (mol. wt. 131.3 g/mole). The weight change of the vessel corresponded to 0.09g (0.7 mmol) Xe (theo. 0.827 mmol) (0.11g) Xe). At -78°C a dark purple solid was present and the HF solution had an orange hue. The reaction was warmed to 0°C and stirred overnight; no further reaction was evident since no more volatile materials were found at -196°C and -97.8°C. The reaction was cooled to -63°C in an attempt to remove only HF from the vessel under vacuum; instead, other volatile materials (probably unreacted CrO_2F_2) transferred simultaneously, resulting in a wine red HF solution in the Kel-F trap. After removal of all volatile materials at -63°C, a deep red solid remained in the reaction vessel. A check for volatile materials at -24°C showed nothing, and only 2 mm pressure of volatile materials were found at 0°C; the 0°C volatile material showed only an absorption characteristic of SiF_4 on the infrared spectrum. The vessel was evacuated at room temperature to a constant weight, yielding 0.28g of a solid product.

Upon opening the vessel in the dry box, a deep red solid was found. The infrared absorptions are listed in Table V. A melting point determination showed that the solid decomposed at 167°C. An iodimetric titration of a 13.3 mg sample of the solid indicated 29% total chromium; thus the molecular weight is 179.2g/mole based on one chromium atom per molecule. The x-ray powder pattern of this material is shown in Table VI.

Discussion

Preparation of $CrOF_3$ by the Action of ClF on CrO_3 at 120°C. $CrOF_3$ is obtained as a powdery solid, ranging from a rose pink to a purple color using this preparative route. The color seems to reflect the purity, and hence stability, of the $CrOF_3$. The rose colored $CrOF_3$ tends to be rather unstable, while the purple $CrOF_3$ is quite stable. For example, the light rose colored $CrOF_3$ turned dark brown quite rapidly, even in the dry box atmosphere, whereas the purple colored $CrOF_3$ discolored very slowly.

In general, it has been found that in reactions of CrO_3 with interhalogen compounds, some of the interhalogen fluorinating agent remains in the $CrOF_3$ product (7, 17). From elemental analysis results it is known that the $CrOF_3$ contains some residual chlorinated contaminant (19). The nature of the chlorinated contaminant is not definitely known, but it has been suggested that the $ClO_2^+CrOF_4^-$ ion pair is the contaminating species (44). If all of the $CrOF_3$ is initially formed as $ClO_2^+CrOF_4^-$, then the net reaction

TABLE V

INFRARED SPECTRUM OF THE PRODUCT FROM THE REACTION OF CrO_2F_2 WITH XeF_2 IN ANHYDROUS HF

Wavenumber (cm^{-1})	Assignment
957 vs	ν_{as} Cr = 0
940 vs	ν_{as} Cr = 0
903 s	ν_s Cr = 0
883 s	ν_s Cr = 0
826 s	Cr-0-Cr
735 s, br	Cr-F
657 vs, br	Cr-F
631 s, br	Cr-F
460 s, vbr	ν Cr-F-Cr
319 m	δ Cr-F and δ Cr-0
307 m	δ Cr-F and δ Cr-0
280 m	δ Cr-F and δ Cr-0
263 m	δ Cr-F and δ Cr-0

TABLE VI

X-RAY POWDER PATTERN OF THE SOLID PRODUCED FROM THE REACTION OF XeF_2 AND CrO_2F_2 IN HF

d(A)	Intensity	d(A)	Intensity
5.07	vw	2.40	m
4.83	vw	2.37	m
4.61	mw	2.30	vvw
4.35	w	2.26	m
4.20	s	2.14	vvw
3.80	m	2.00	vw
3.75	m	1.963	w
3.57	vw	1.857	vvw
3.43	s	1.835	vw
3.35	s	1.741	w
3.18	w	1.713	vvw
2.87	m	1.499	vvw
2.64	vvw	1.431	vvw
2.59	vvw	1.398	vw
2.48	vvw	1.376	w
2.44	vvw	1.351	mw

s = strong, m = medium, mw = medium weak, w = weak, vw = very weak, vvw = very very weak will be:

III-18 $8ClF + 2CrO_3 \longrightarrow 2ClO_2^+CrOF_4^- + 3Cl_2$

This equation is in good agreement with what is experimentally observed. The stoichiometry of 4ClF to $1CrO_3$ is fully supported by the observation that at least a 4:1 excess of ClF is required to obtain high yields of $CrOF_3$ (19), and by the observation of Cl_2 as a volatile product in the reaction. The equation also accounts for the fact that no F_2 is observed as a product; the formation of ClF from Cl_2 and F_2 is precluded under the reaction conditions employed. The equation, however, fails to predict the formation of O_2 as a product, and O_2 is an experimentally observed product.

The final step in the reaction would have to involve the thermal decomposition of $ClO_2^+CrOF_4^-$ to yield $CrOF_3$:

III-19 $ClO_2^+CrOF_4^- \longrightarrow CrOF_3 + ClO_2F$

Equation 19 accounts for the experimentally observed ClO_2F, and at the temperature involved may also account for the observed O_2; ClO_2F is thought to exist in equilibrium with ClO_2 and F_2 as in equation 20 (47),

III-20 $2ClO_2F \longrightarrow 2ClO_2 + F_2$

and the thermal instability of ClO_2 is well known (48). Regardless of whether or not $CrOF_3$ forms initially as $ClO_2^+CrOF_4^-$, the resulting crude product contains 3.32% to 5.52% chlorine by weight (19).

It has been found that pure $CrOF_3$ can be produced from the crude $CrOF_3$ by multiple treatments of the solid with fluorine at 120°C. It is interesting that the only volatile material identified from these treatments (other than F_2) is ClO_2F. What is also of interest is that it has been found in the present work that treating the crude $CrOF_3$ by multiple heatings with O_2 also results in releasing ClO_2F as the only identified volatile material other than O_2. It was found, however, that even after no more ClO_2F was obtained after multiple oxygen treatments, further treatment of the same material with fluorine resulted in the formation (or removal) of some residual ClO_2F; and so it appears that the use of fluorine is ultimately required in the purification process.

The chemical means by which most of the chlorine containing contaminant is removed by multiple treatments with F_2 or O_2 are not obvious, regardless of whether the contaminant is ClF or ClO_2F. It is found, however, that the only infrared active volatile material at -17°C obtained from these treatments is ClO_2F. ClO_2F could possibly be produced from reactions 26 and 27, but the fact that

III-26 $F_2 + 2ClO_2{}^+CrOF_4{}^- \longrightarrow 2ClO_2F + 2CrOF_4$

III-27 $xO_2 + CrOF_3 \cdot xClF \longrightarrow CrOF_3 + xClO_2F$

ClO_2F is produced in both treatment methods, using presumably identical crude $CrOF_3$, suggests that the removal of the contaminant may simply involve a forced displacement brought about by collisions of the F_2 or O_2 molecules with the impure $CrOF_3$.

With regard to the formation of $CrOF_3$ from CrO_3, it is likely that initially two oxygen atoms are replaced by four fluorine atoms to produce $CrOF_4$; Edwards et al., proposed this kind of stepwise replacement of one oxygen for two fluorine atoms in their preparation of $CrOF_4$ from CrO_3 and F_2 (14). It is tempting to attribute strong absorptions, centered at about 1085cm^{-1} in the infrared spectrum of the room temperature volatile products formed from the O_2 and F_2 treatments of crude $CrOF_3$, to $CrOF_4$ (the calculated frequency due to ν Cr=0 is 1080 cm^{-1} (49)), but this absorption doesn't occur concommitantly with any absorptions above 300cm^{-1} which can be attributed to ν Cr-F vibrational modes. Therefore, it must be assumed that any $CrOF_4$ produced is ultimately reduced to $CrOF_3$.

The infrared spectrum of $CrOF_3$, along with spectral assignments, is tabulated in Table VII. The strong absorption at 1000cm^{-1} can be unambiguously assigned to a ν Cr=0 vibration, absorptions in the 600cm^{-1} to 740cm^{-1} region are assigned to terminal ν Cr-F vibrations, and the absorptions at 565cm^{-1}, and possibly those at 512cm^{-1} and 480cm^{-1} are thought to be due to a ν Cr-F-Cr vibration (18). The terminal Cr=0 absorption is in good agreement with those found for VOF_3 (50) and $MoOF_3$ (51); the terminal M=0 stretching frequencies for these two complexes occur at 1039cm^{-1} (Raman) and 1000cm^{-1} (infrared), respectively. The

TABLE VII

INFRARED SPECTRUM OF $CrOF_3$

Wavenumber(cm^{-1})	Assignment
1000 s	ν Cr=0
785 w	512 + 270
718 s	ν Cr-F
682 s	ν Cr-F
600 vs	ν Cr-F
565 s	ν Cr-F-Cr
512 s	ν Cr-F-Cr
480 m	ν Cr-F-Cr
380 w	δ Cr-F
350 vw	δ Cr-F
330 w	δ Cr-F
270 m	δ Cr-F

absorptions assigned as νCr-F-Cr bridging vibrations are in good agreement with infrared active M-F-M vibrational modes found in solid CrO_2F_2 at $540cm^{-1}$ (52), in solid $ReOF_4$ at $540cm^{-1}$, (53), and in NbF_5 and TaF_5 at $541cm^{-1}$ and $479cm^{-1}$, respectively (52).

The spectroscopic evidence thus suggests a dimeric or polymeric structure for $CrOF_3$, with Cr-F-Cr bridges between each $CrOF_3$ unit, and with terminal Cr=0 and Cr-F bonds. The physical properties of $CrOF_3$, its nonvolatility, its very low solubility even in high dielectric solvents such as HF, and its high melting point, fully support the infrared evidence indicating a polymeric structure with extensive fluorine bridging. The proposed structure of $CrOF_3$ is shown in Figure 10, and is analogous to that found for VOF_3 (54).

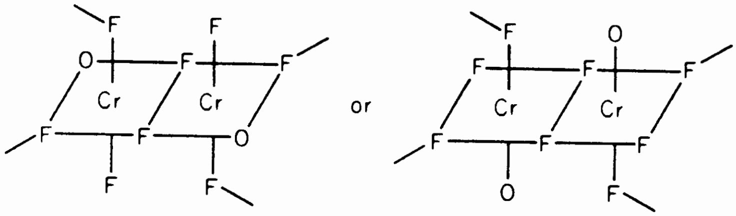


Figure 10. Proposed structure of $CrOF_3$.

Preparation of $CrOF_3$ by the Reaction of XeF_2 With CrO_2F_2. The $CrOF_3$ produced by the reaction of XeF_2 with CrO_2F_2 appears to be identical to the purest $CrOF_3$ prepared from CrO_3 and ClF, and therefore represents a superior synthetic route to $CrOF_3$, for which interhalogen contamination is precluded.

The infrared spectrum is identical to that previously obtained for dark purple $CrOF_3$, with the exception of two of the bands at 357 and 380cm^{-1} (assigned as δ Cr-F vibrations) which are both very weak for the $CrOF_3$ prepared by XeF_2 and CrO_2F_2. Based on this infrared evidence, and on similar physical properties such as a high melting point, lack of volatility, and lack of solubility in virtually every solvent tested (with the possible exception of HF in which $CrOF_3$ may be sparingly soluble), the $CrOF_3$ prepared by this new method is assumed to have the same solid state structure as in Figure 10.

The use of XeF_2 as a fluorinating agent has received a great deal of attention in the fairly recent literature (55). Disappointingly, the reaction of XeF_2 and CrO_2F_2 did not yield $CrOF_4$, even with XeF_2 and CrO_2F_2 in a 1:1 stoichiometric ratio. $CrOF_4$ may well be formed as an intermediate as in equation 21, followed by the decomposition of $CrOF_4$ to $CrOF_3$ and F_2. At the high temperature of the reaction

III-21 $XeF_2 + CrO_3 \longrightarrow CrOF_4 + Xe + O_2$

the F_2 could react with Xe to reform XeF_2 (XeF_2 is formed from the elements at 250°C), and thus a cycle is established until all the fluorine is consumed. It is also possible that a fluorine bridged intermediate may be formed as in Figure 11.

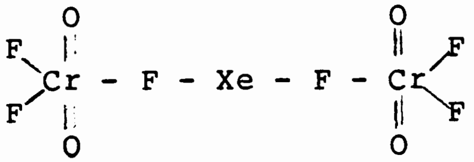


Figure 11. Intermediate fluorine bridged structure in the formation of $CrOF_3$.

A fluorine bridged structure such as this has been observed by x-ray crystalography in XeF_2WOF_4 (56), and by ^{19}F and ^{129}Xe NMR spectroscopy in $XeF_2 \cdot MOF_4$, $XeF_2 \cdot 2MOF_4$, and $XeF_2 \cdot nMOF_4$ (M = Mo, W; n = 1-4) (55a, 57). The $[FXe]^+[Sb_2F_{11}]^-$ ion pair is an often cited example of this as well (60). However, it's perhaps unlikely that there would be much ionic character in the proposed $XeF_2 \cdot 2CrO_2F_2$ intermediate; Holloway and Schrobilgen found for example that WOF_4 is superior to $MoOF_4$ as a fluoride acceptor (55a), and thus one might expect CrO_2F_2 to be an even weaker fluoride acceptor. It should be pointed out though that NMR analysis has proven the existence of Xe-F-M bridging for some strong Lewis acid metal species only at low temperatures, while at room temperature an ionized form is favored (55c, d, e, 57). So it would be incorrect to assume that the proposed intermediate doesn't have some degree of ionic character at the high temperature at which the reaction is effected; the $FXe^+CrO_2F_3^-$ ion pair, for example, could conceivably be formed. The $XeF_2 \cdot 2CrO_2F_2$ intermediate could then decompose, yielding $CrOF_3$, Xe, and O_2.

III-22 $XeF_2 \cdot 2CrO_2F_2 \longrightarrow 2CrOF_3 + Xe + O_2$

Regardless of whether such an intermediate is formed and how it decomposes, the overall reaction of XeF_2 and CrO_2F_2 is favored by the accompanying increase in entropy.

The reaction of XeF_2 and CrO_2F_2 was nearly nonexistent at reaction temperatures less than 250°C, and yields of $CrOF_3$ decreased as the temperature was raised beyond 290°C. The optimal reaction temperature seems to be between 265°C and 275°C. The temperature dependence of the reaction is interesting in that the equilibrium of XeF_2 with Xe and F_2 is rapidly established only at temperatures exceeding 250°C.

An x-ray crystal study of the $CrOF_3$ produced in this reaction is currently underway, and the results are anxiously awaited in order that the detailed structure of this pentavalent chromium complex can be established.

<u>Preparation of Cr(V) Metal Fluoride Salts of Group IA and IIA Metal Fluorides</u>. The products of the reactions of $CrOF_3$ with NaF, KF, and MgF_2, were all obtained as off-white to pale green or yellow solids, and all exhibited characteristic infrared absorptions attributable to νCr=0 and νCr-F. The infrared spectra of these salts, tentatively formulated as Na_2CrOF_5, K_2CrOF_5, $MgCrOF_5$, and $Mg(CrOF_4)_2$, as well as those of $KCrOF_4$ (19, 18) and $(Et_4N)_2CrOF_5$ (3), are compared in Table VIII.

Both the Na and K salts were formed initially as HF adducts; the infrared spectra showed characteristic absorp-

TABLE VIII

Cr=0 AND Cr-F INFRARED ABSORPTION FREQUENCIES FOR Na_2CrOF_5, K_2CrOF_5, $MgCrOF_5$, $Mg(CrOF_4)_2$, $KCrOF_4$, and $(Et_4N)_2CrOF_5$

Complex	νCr=0(cm^{-1})	νCr-F(cm^{-1})
$(Et_4N)_2CrOF_5$	960, 890	480, 450
Na_2CrOF_5	984, 952	650, 500
K_2CrOF_5	993, 956	613, 594, 533
$MgCrOF_5$	1003, 985	683, 649, 604
$Mg\cdot CrOF_4$	1006, 987	696, 648, 603
$KCrOF_4$	1020, 982	640, 500

tions for the HF_2^- anion in each case. Interestingly, the infrared spectra of the magnesium salts did not indicate the presence of either the HF_2^- anion, or discrete HF molecules as impurities. In all cases, however, the vessel weights after removal of HF solvent at room temperature corresponded to greater than 100% yields, indicating incomplete removal of HF. All of the HF, present as HF_2^-, was removed by prolonged heating under vacuum, resulting in final weights which were only slightly greater than expected for 100% yield. Complete removal of volatile impurities by heating to high temperatures under vacuum was usually precluded by product decomposition; however, Na_2CrOF_5 was heated to 220°C without apparent decomposition.

The impurity (or impurities) which contribute to the poor elemental analysis of the Na and Mg salts is probably not HF or HF_2^-; the elemental analyses show that the salts are 4 to 19.4% deficient in fluorine. Incomplete drying of the starting NaF and MgF_2 could have resulted in some H_2O contamination, and unknown impurities in the HF could have also been present. Elemental analysis of the $CrOF_3$ used in these reactions was not obtained, and so its purity can not be guaranteed either. Complicated and/or unexpected reactions in these systems are other possible causes for the poor elemental analyses obtained for these compounds.

For all of these oxyfluoride salts, the Cr=O stretching vibration is split into two absorptions; this has been explained for $CsVOF_4$ as being due to a solid state effect (59), and for $(Et_4N)_2CrOF_5$ as perhaps being due to having a tightly bound fluoride trans to the oxygen giving rise to antisymmetrical and symmetrical vibrations (13).

The νCr-F spectral region is unfortunately not highly resolved for most of these salts. Therefore, determining the symmetry of these salts is difficult. The point group symmetry of $KCrOF_4$ was taken to be C_{4v} based on the requirement of only six infrared active absorptions for this symmetry versus eleven active absorptions for C_{2v} symmetry (19); and from similar spectral characteristics to $CsVOF_4$ (18) for which C_{4v} symmetry is also assumed (59). This is consistent with the fact that many oxotetrachlorochromate (V) salts have been assumed to be of C_{4v} symmetry (4), as has been confirmed for $[AsPh_4][CrOCl_4]$ (60). Similarly, the magnesium salt formulated as $Mg(CrOF_4)_2$ is likely to have square pyramidal geometry (C_{4v} symmetry); the salt shows only five well resolved infrared absorptions, and none of the νCr-F absorptions are in the region attributed to bridging modes.

The salts formulated as Na_2CrOF_5, K_2CrOF_5, and $MgCrOF_5$, are most likely of octahedral geometry and C_{4v} symmetry like that formed for $ReOF_5$, IOF_5, and $OsOF_5$ (61). The νCr-F spectral region for these new Cr(V) salts, by analogy to $ReOF_5$, IOF_5, and $OsOF_5$, is composed of the derivatives of the O_h fundamental modes ν_1, ν_2, and ν_3.

The infrared spectra of K_2CrOF_5, $ReOF_5$, and $OsOF_5$, are listed in Table IX. All of the fundamental vibrational modes of K_2CrOF_5 are closely comparable to $ReOF_5$ and $OsOF_5$, thus supporting the assignment of C_{4v} symmetry to K_2CrOF_5. None of the $CrOF_5^{2-}$ salts show infrared absorptions which can be unambiguously assigned to ν Cr-F-Cr bridging modes.

Reaction of CrO_2F_2 and XeF_2 in Anhydrous HF. Unlike the reactions of MoO_2F_2 and WO_2F_2 with XeF_2 in anhydrous HF which yielded the metal oxide tetrafluorides (46), the product of the reaction of CrO_2F_2 with XeF_2 in HF was disappointingly not $CrOF_4$. The infrared spectrum exhibits absorptions at 957cm^{-1} and 940cm^{-1} which are assigned as ν Cr=0 vibrational modes; these, however, are well below the 1080cm^{-1} expected for $CrOF_4$ (49). The absorptions at 903cm^{-1} and 883cm^{-1} are possibly due to ν_{sym} Cr=0 vibrational modes; they are likely too high to be due to ν Cr-0-Cr vibrations. The absorption at 826cm^{-1} is in the region typical for bridging Cr-0-Cr vibrations, which suggests a possible dimeric or polymeric structure. The absorptions between 490cm^{-1} and 750cm^{-1} are attributable to ν Cr-F vibrations. Due to the poor resolution of the region between 490cm^{-1} and 550cm^{-1}, it is not possible to confirm the existence of fluorine bridging; the broad shoulder at 500cm^{-1} could conceivably be due to ν Cr-F-Cr.

The fact that no volatile materials were found at -196°C (i.e. O_2 and F_2 were not reaction products) implies

TABLE IX

INFRARED SPECTRA OF K_2CrOF_5, $ReOF_5$, AND $OsOF_5$ IN CM^{-1}

K_2CrOF_5	$ReOF_5$	$OsOF_5$	Assignment
993	992	960	ν_1 M-O
956			
613	742	710	ν_2 M-F (sym)
594	711	700	ν_8 M-F bend
533	649	640	ν_3 F-M-F bend

that the CrO_2F_2 remained in tact, and the removal of 0.09g of volatile materials at -97.8°C accounts quantitatively, within experimental error, for all of the xenon originally present as XeF_2. Based on the final weight, this corresponds to 2.45 CrO_2F_2 to 1 F_2 assuming that the final product does not contain coordinated HF, an assumption which is not unreasonable since no glass attack was evident during the melting point determination.

Although the infrared spectrum possibly supports oxygen and/or fluorine bridging, the physical properties (i.e. solubility and melting point) are not indicative of any extensive polymerization.

It is not possible to hypothesize further on the nature of this product. Because it was primarily intended to be a small scale "test" reaction, only a small sample (13.3 mg) was used for the iodimetric titration, resulting in what is likely to be an inaccurate percent chromium determination, and no elemental analysis was obtained. The compound has proven to be quite stable, remaining unchanged after being stored for two years in a sealed Pyrex glass tube.

CHAPTER IV

PREPARATION OF NEW Cr(VI) HETEROCYCLIC COMPLEXES

Introduction

The usefulness of hexavalent chromium has long been recognized in organic synthetic chemistry; as an oxidizing agent, it is able to convert alcohols to ketones, aldehydes, and carboxylic acids. The oxidizing characteristics of hexavalent chromium can be significantly altered by the types of ligands which surround the central metal atom. By changing the ligands, one should be able to both regulate the activity of the oxidizing agent and perhaps impart some degree of stereoselectivity at the same time.

One of the first examples of a hexavalent chromium complex which functioned as a relatively mild oxidizing agent, but showed no specific stereoselectivity, was the dipyridine-chromium(VI) oxide complex (29). However, the use of pyridine as the solvent and the extremely hydroscopic nature of the chromium(VI) complex posed technical difficulties in the preparation and work up of oxidation reactions.

A complex which is much more easily handled both in its preparation and use is the pyridinium chlorochromate complex (32). Pyridinium chlorochromate (PCC) is easily prepared by the addition of pyridine to a solution of CrO_3 in 6M HCl. The complex thus formed is obtained in good yields by filtration of the solid with subsequent drying under vacuum. The yellow orange PCC is air stable, and neither PCC nor its reduced products are soluble in CH_2Cl_2; this makes CH_2Cl_2 an ideal solvent in which to run oxidation reactions. Since its introduction as an oxidizing agent, PCC has often been employed as an oxidizing agent in organic synthesis (62, 63).

Although PCC has received widespread application as an oxidizing agent, there still exists a need for oxidizing agents which can function in a unique stereochemical capacity. Recent examples include the bipyridinium chlorochromate complex (35). Both reagents behave as mild oxidizing agents, are insoluble in CH_2Cl_2, and are easily separated from the desired carbonyl products.

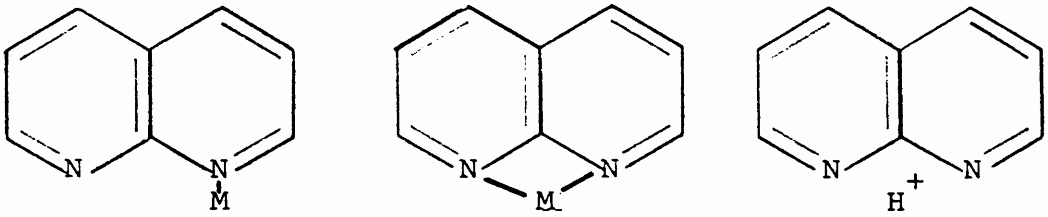
As is evident from the current literature, there is a large interest in the preparation of complexes which act as selective oxidizing agents. Unfortunately, most of these reports are primarily concerned with the oxidizing capabilities of the complexes, while the characterization of the complexes has received rather superficial treatment. With a particular interest in the characterization of new Cr(VI) complexes, the heterocyclic ring systems naphthyridine, pyrazine, pyrazine-N-oxide, and tripyridine have been reacted with CrO_3 under a variety of conditions. The new Cr(VI) complexes have been fully studied by infrared and ultraviolet and visible spectroscopy, x-ray powder photography, elemental analysis, and chemical and physical properties (i.e. solubility, melting point, volatility, stability towards light and moisture). A summary of these complexes and their proposed structures are presented in Table X and Figure 36. A study of the oxidizing capabilities of these new complexes with selected alcohols was also undertaken, and these results are discussed in Chapter V.

There are several means by which naphthyridine can form complexes with metals; these are illustrated in Figure 12. In example I, the bonding of the naphthyridine as a monodentate ligand to the metal can be viewed as a simple donation of the nitrogen lone pair electrons to an empty metal d orbital; thus a dative bond is formed between the Lewis base naphthyridine and the Lewis acid metal center. In example II, the naphthyridine acts as a bidentate Lewis base ligand. Complexes of this type have been fully characterized by x-ray crystalography (64). In example III, the naphthyridine acts as a monovalent cation; the naphthyridinium cation can thus form an ionic interaction with an appropriate anion. No evidence was found for diprotonated naphthyridine.

TABLE X

NEW HETEROCYCLIC CHROMIUM(VI) COMPLEXES

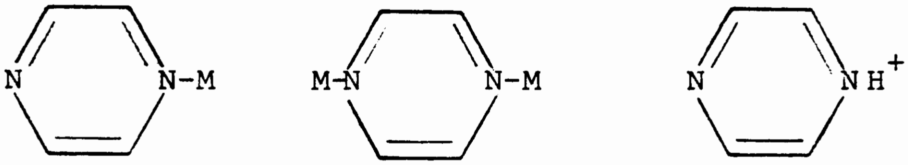
$(C_8H_6N_2H)CrO_3Cl$	NapCC	Naphthyridinium Chlorochromate
$(C_4H_4N_2H)CrO_3Cl$	PzCC	Pyrazinium Chlorochromate
$(C_4H_4N_2OH)CrO_3Cl$	PzOCC	Pyrazinium-N-oxide Chlorochromate
$(C_{15}H_{13}N_3Cl)CrO_3Cl$	TPCC	Tripyridinium-hydrochloride Chlorochromate
$(C_8H_6N_2H)_2Cr_2O_7$	NapDC	Naphthyridinium Dichromate
$(C_4H_4N_2H)_2Cr_3O_{10}$	PzTC	Pyrazinium Trichromate
$(C_4H_4N_2CrO_3)n$	PzCA	Pyrazine Chromic Anhydride



I II III

Figure 12. Modes of bonding to metals by naphthyridine, and protonated form

Another heterocyclic compound which exhibits varying modes of complex formation with metals is pyrazine (1,4.-diazene). Because pyrazine also has two nitrogen atoms in its ring structure, it can potentially use both lone pairs of electrons in complex formation. The different means by which pyrazine can form complexes with metals are shown in Figure 13. In examples IV and V the pyrazine acts as a Lewis base and forms dative bonds to the metal center. Examples of these types of complexes are numerous in the literature (65). Pyrazine can also exist as a monoprotonated cation and form an ionic bond with an appropriate anion as shown in example VI.



IV V VI

Figure 13. Modes of bonding to metals by pyrazine, and protonated form

The mono-N-oxide of pyrazine, pyrazine-N-oxide was also studied in reactions with CrO_3. The structure of pyrazine-N-oxide is shown in Figure 14.

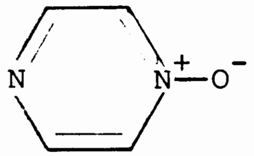
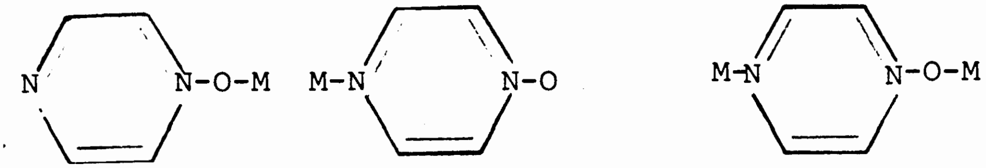


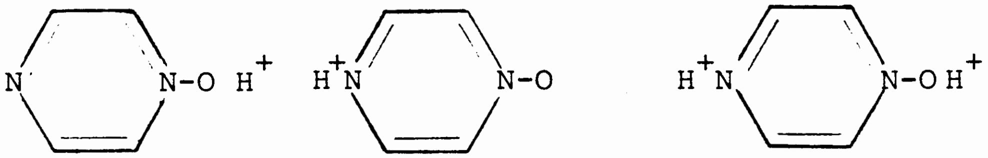
Figure 14. Structure of pyrazine-N-oxide

This heterocycle is unique in that it has lone pairs of electrons on both the neutral nitrogen atom and the oxygen atom; one would expect that both of these lone pairs of electrons could function in a Lewis base capacity. Therefore one might expect to find complexes of this heterocycle in which the metal-ligand bond could be either through the oxygen or the neutral nitrogen with pyrazine-N-oxide acting as an unidentate ligand, or that the pyrazine-N-oxide might function as a bridging bidentate ligand by bonding through both the nitrogen and oxygen. These various coordination schemes are illustrated in Figure 15. All three types of these complexes are known to exist (66). Insofar as ionic complexes formed between a protonated pyrazine-N-oxide and a metalate anion are concerned, three protonated forms of pyrazine-N-oxide are conceivable; these are illustrated in Figure 16.



VI VII IX

Figure 15. Modes of bonding to metals by pyrazine-N-oxide.



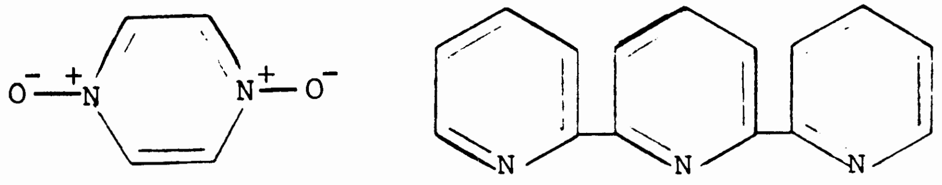
X XI XII

Figure 16. Protonated forms of pyrazine-N-oxide

There is some disagreement in the literature as to whether the nitrogen or the oxygen is protonated first in pyrazine-N-oxide. Two reports suggest that the nitrogen atom is first to be protonated (67, 68), while another suggests that the oxygen is first to be protonated, when H_2SO_4 is used as the acid (69). One of these investigations did find that pyrazine-di-N-oxide was only slowly protonated compared to the pyrazine-N-oxide, and it may be reasonable to assume therefore that the nitrogen atom is protonated first.

Other heterocyclic ring systems studied as potential ligands for cations in their protonated forms include pyrazine-di-N-oxide and tripyridine; these are shown in

Figure 17.



(a) (b)

Figure 17. a=pyrazine-di-N-oxide, b=tripyridine

Experimental.

Reactions of Nitrogen Containing Heterocyclic Ring Systems with Chromium Trioxide in Acidic Aqueous Media

In an aqueous solution containing HCl, the chlorochromate ion is formed upon addition of chromium trioxide through the bichromate ion (70).

IV-1 $HCrO_4^- + H^+ + Cl^- \longrightarrow CrO_3Cl^- + H_2O$

An excess of HCl should therefore assure that the reaction lies far to the right. Also, the formation of H_2O in this reaction provides a driving force favoring the chlorochromate ion. Using Pearson's rules of hard and soft acids and bases (71), and the stability of complexes formed between acids and bases, one would expect that stable complexes containing the hard base chlorochromate ion could be formed in the presence of hard or borderline acids; both the hard acid K^+ and the borderline acid $C_5H_5NH^+$ (72) form the well-known $KCrO_3Cl$ and $C_5H_5NHCrO_3Cl$ complexes, respectively.

Reaction of Naphthyridine, Chromium Trioxide, and HCl

in Water. Naphthyridine, (1.60 mmol), was thoroughly dissolved in 1 ml H_2O containing 0.17 ml (2.04 mmol) 12 M HCl in a 25 ml round bottom flash equipped with a magnetic stir bar, and the solution was cooled to 0°C. A second solution at room temperature containing 170.2 mg (1.70 mmol) CrO_3 and 0.35 ml (2.1 mmol) 6 M HCl in 2 ml H_2O was added dropwise over a 10 min. period to the naphthyridine solution; the naphthyridine solution was held at 0°C and stirred throughout the addition of the chlorochromate solution. An orange solid precipitated out of solution within 5 to 10 seconds of the initial contact of the two solutions. Following the addition of the chlorochromate solution the temperature was maintained at 0°C and the solution was stirred for 60 min. The orange powdered solid was filtered by suction on a sintered glass funnel, and this solid was twice recrystalized from a minimal amount of acidified water. Slow cooling of the water solution resulted in fine needle-like crystals of naphthyridinium chlorochromate; the bright orange crystals were dried under vacuum for 48 hrs. (10^{-3}torr). Yield, 0.3535 g (67.3%); m.p. 137-139°C. Analysis calculated for $C_8H_7N_2CrO_3Cl$: C, 36.04; H, 2.65; N, 10.51; Cl, 13.30; Cr, 19.50. Found: C, 36.08; H, 2.71; N, 10.46; Cl, 13.25; Cr, 19.48.

The x-ray powder pattern is shown in Table XI and the infrared spectrum between 1600 and 200cm^{-1}, and the uv/vis spectrum (λ_{max}(nm) = 455 (w, br), 365 (m), 308 (s), 301 (s))

TABLE XI

X-RAY POWDER PATTERN OF $(C_8H_6N_2H)CrO_3Cl$

d(A)	Intensity	d(a)	Intensity
6.70	vw	3.17	ms
6.44	w	3.07	vw
6.08	m	2.89	mw
5.75	s	2.77	m
5.18	vw	2.44	vw
4.70	m	2.33	w
4.40	m	2.14	w
4.28	m, br	2.09	w
3.95	ms	1.92	vw
3.55	vs	1.82	vw

vs = very strong, s = strong, m = medium, mw = medium weak, w = weak, vw = very weak, br = broad are shown in Figure 18 and 19 respectively. The positions of the infrared absorptions and the mode assigned to each are listed in Table XII; the spectral assignments corresponding to the naphthyridine ring in the complex are based on those for pure naphthyridine (73). NapCC is soluble in CH_3CN, H_2O, Pyridine, DMSO; insoluble in Et_2O, CH_2Cl_2, CCl_4. The complex is nonhygroscopic, and stable for at least six months when stored in the dark.

Reaction of Pyrazine, Chromium Trioxide, and HCl in Water. Pyrazine, (2.24 mmol), was thoroughly dissolved in 4 ml H_2O containing 0.19 ml (2.28 mmol) 12 M HCl in a 25 ml round bottom flask equipped with a Teflon coated magnetic stir bar, and the solution was cooled to 0°C. A second solution at room temperature containing 230.7 mg (2.31 mmol) CrO_3 and 0.2 ml (2.4 mmol) 12 M HCl in 2 ml H_2O was added dropwise to the $C_4H_4N_2$ solution. An orange solid formed immediately upon contact of the two solutions. After addition of half of the CrO_3 solution, the 0°C solution was stirred for 5 min before the remaining solution was added. The solution was then stirred for 0.33 hr. at 0°C. The orange solid was collected on a sintered glass funnel, and twice recrystallized from a minimal amount of acidified H_2O, yielding bright orange needle-like crystals of pyrazinium chlorochromate (PzCC). The solid was dried under vacuum (10^{-3}torr) for 24 hours at room temperature. Yield, 0.2938g (61%); m.p. 148-150°C. Analysis calculated for

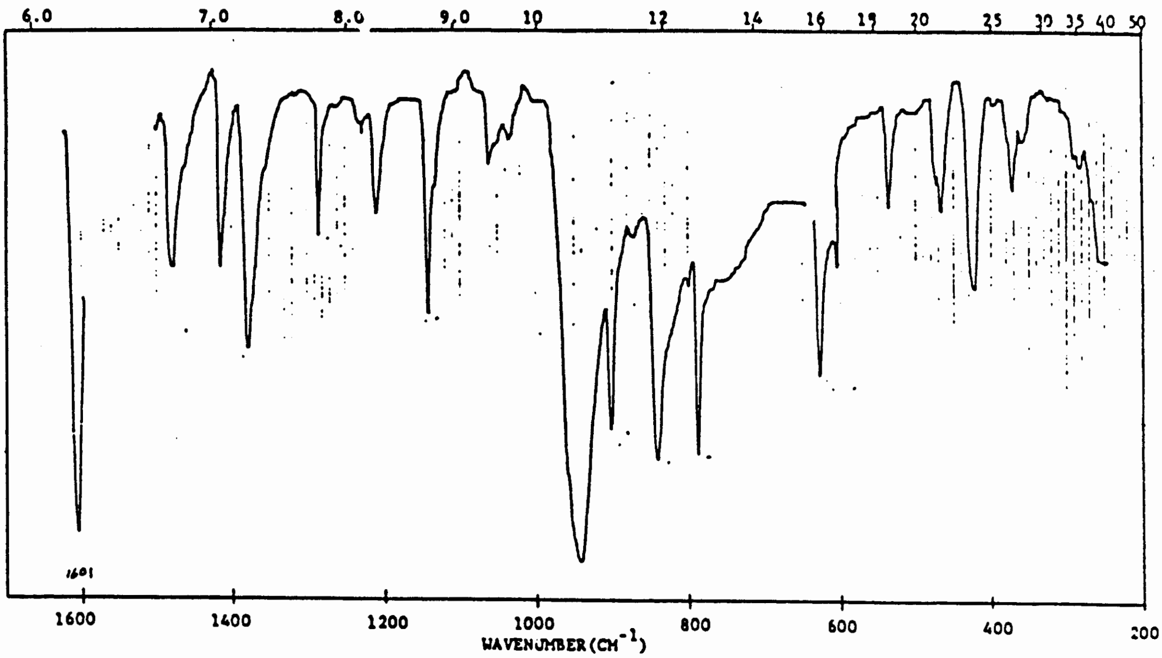


FIGURE 18. Infrared spectrum of $(C_8H_6N_2H)CrO_3Cl$

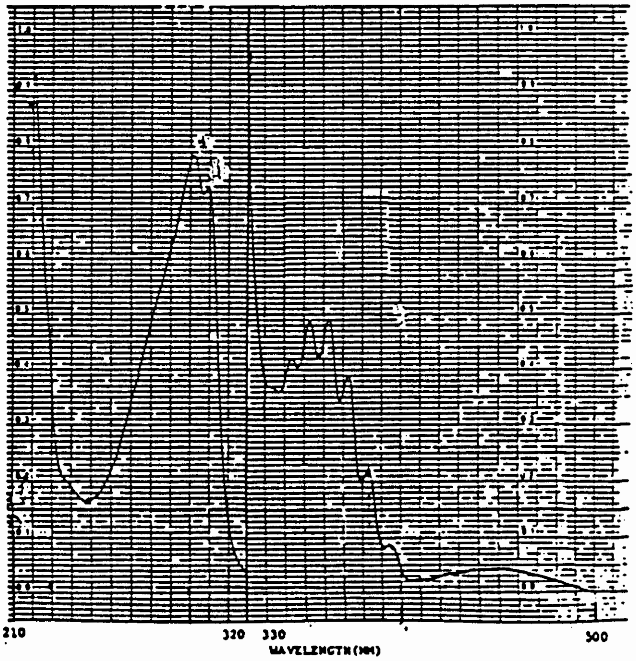


FIGURE 19. UV/VIS spectrum of $(C_8H_6N_2H)CrO_3Cl$

TABLE XII

INFRARED SPECTRUM OF $(C_8H_7N_2)CrO_3Cl$ IN CM^{-1}

$(C_8H_7N_2)CrO_3Cl$	Assignment	$(C_8H_7N_2)CrO_3Cl$	Assignment
3070 mw	CH st	1031 w	1651-531=1035?
3033 mw	CH st	937 vs	ν_{as} Cr O
1651 m	skel st	898 s	ν_s Cr O
1628 m	skel st	865 m	1651-783=868
1605 ms	skel st	836 s	CH op be
1566 w	skel st	783 s	CH op be
1546 w	skel st	642 w	
1475 m	skel st	623 ms	
1412 m	skel st	531 mw	
1371 ms	CH ip be	462 mw	
1281 m	CH ip be	423 m	ν Cr Cl
1206 m	CH ip be	368 mw	
1139 ms	skel be		
1060 w	2 x 531 = 1062?		

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, Ch st = CH stretch, skel st = skeletal stretch, CH ip be = CH in-plane bend, CH op be = CH out-of-plane bend

$C_4H_5N_2O_3ClCr$: C, 22.19; H, 2.33; N, 12.94; Cl, 16.37; Cr. 24.01. Found: C, 22.32; H, 2.34; N, 13.00; Cl, 16.27; Cr, 24.05.

The x-ray powder pattern is shown in Table XIII, and the infrared spectrum between 1700 and 200cm^{-1}, and uv/vis spectrum (λ_{max} (nm) = 454 (m, br), 364 (m), 312 (m, br), 267 (s), 261 (s), 255 (s), 248 (s, sh)) are shown in Figures 20 and 21 respectively. The positions of the infrared absorptions and the mode assigned to each are listed in Table XIV; the spectral assignments associated with the pyrazine ring in the complex are based on those for pure pyrazine (74, 75). PzCC is insoluble in CH_2Cl_2, CCl_4, and $(CH_3CH_2)_2O$, and soluble in H_2O and CH_3CN. While PzCC readily dissolves in pyridine, it was found that pyridine readily exchanges with pyrazine to form the pyridinium chlorochromate complex; this was determined by infrared and uv studies. Finally, PzCC reacts very exothermally with dimethylsulfoxide. The complex is nonhygroscopic and is stable for at least six months when stored in the dark.

Reaction of Pyrazine-N-oxide, Chromium Trioxide, and HCl In Water (19). Pyrazine-N-oxide, (5.2 mmol), was thoroughly dissolved in 2 ml (12 mmol) 6N HCl and added dropwise with stirring to a solution of 1.35g (13.5 mmol) CrO_3 in 2 ml (12.0 mmol) 6N HCl. An orange solid was formed and collected on a sintered glass funnel. The filtrate was collected and cooled to -10°C after which more solid was

TABLE XIII

X-RAY POWDER PATTERN OF $(C_4H_4N_2H)CrO_3Cl$

d(A)	Intensity	d(A)	Intensity
6.38	w	2.36	ms, br
5.68	ms	2.12	m
5.08	vs	2.018	mw, br
4.46	m	1.975	mw
4.16	w	1.939	w
4.04	vs	1.891	m
3.79	s	1.829	vw
3.67	vw	1.800	m
3.53	m	1.774	m
3.28	w	1.993	m
3.19	vs	1.646	m
3.03	w	1.627	m
2.89	ms	1.596	m
2.82	ms	1.517	m
2.74	ms	1.454	mw
2.54	vs	1.417	mw
2.46	s		

s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, br = broad

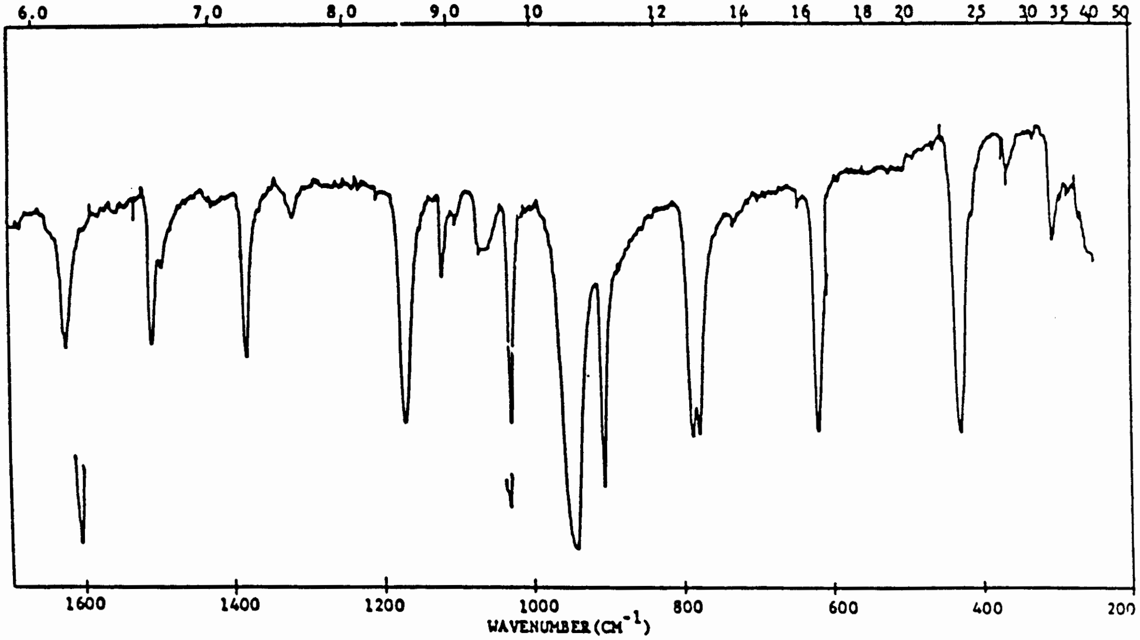


FIGURE 20. Infrared spectrum of $(C_4H_5N_2)CrO_3Cl$

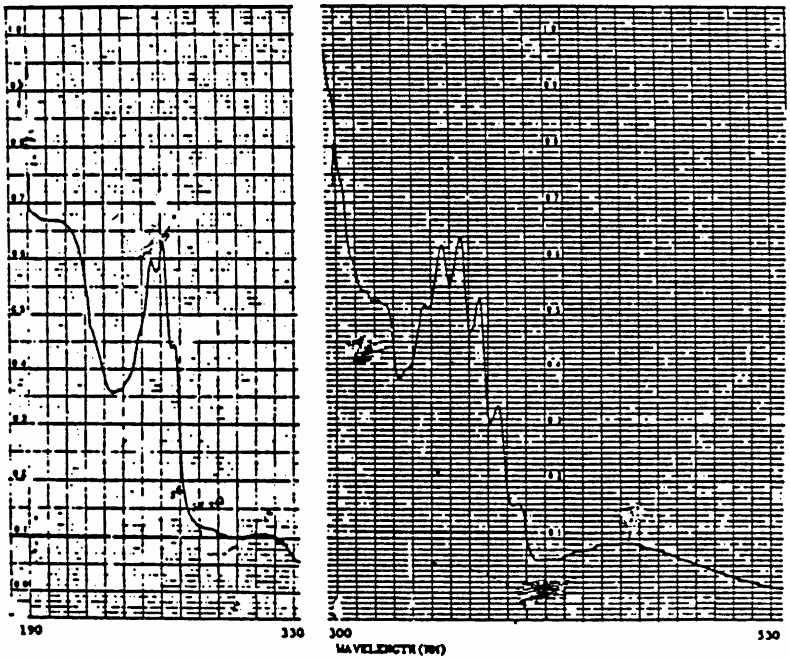


FIGURE 21. UV/VIS spectrum of $(C_4H_5N_2)CrO_3Cl$

TABLE XIV

INFRARED SPECTRUM OF $C_4H_5N_2CrO_3Cl$ IN CM^{-1}

$C_4H_5N_2CrO_3Cl$	Assignment	$C_4H_5N_2CrO_3Cl$	Assignment
3120 w	CH st	1116 w	CH be?
3082 mw	CH st	1054 w	CH be
3054 m	CH st	1023 m	ring or CH/be
2960 m	?	938 vs	ν_{as} CrO
2700 w, br	3054-364=2690?	901 s	ν_{s} CrO
1618 m	ring	782 s	CH def
1501 m	ring	772 s	CH def
1316 m	ring	613 s	ring
1164 s	ring	423 s	ν Cr Cl
		364 w	ring

vs = very strong, s = strong, m = medium, mw = medium weak, w = weak, br = broad, CH st = SH stretch, CH def = CH deformation, CH be = CH bend formed and subsequently collected in the same manner. The combined solid was dried under vacuum (10^{-3}torr) for 12-15 hr. Yield, 0.851g (70%); m.p. 94°C. Analysis calculated for $C_4H_5N_2O_4ClCr$: C, 20.66; H, 2.15; N, 12.04; Cl, 15.25; Cr, 22.36. Found: C, 20.70; H, 2.34; N, 12.08; Cl, 15.46; Cr, 22.11.

The x-ray powder pattern is shown in Table XV, and the infrared spectrum (1700 - 200cm^{-1}) and the uv/vis spectrum are shown in Figures 22 and 23, respectively. The positions of the infrared absorptions and the mode associated with each are listed in Table XVI; the N-O vibrations have been assigned based on those in free pyrazine-N-oxide (66). The compound is highly soluble in H_2O, $(CH_3)_2CO$, C_5H_5N, and CH_3CN; slightly soluble in $CHCl_3$, and insoluble in $(CH_3CH_2)O$, $C_6H_5CH_3$, and CH_2Cl_2. The complex is nonhygroscopic, and is stable for at least six months when stored in the dark.

Reaction of 2'2'2-Tripyridine, Chromium, Trioxide, and HCl in Water. Tripyridine, (2.1 mmol), was thoroughly dissolved in 1 ml (6 mmol) 6N HCl and added dropwise to a solution containing 210 mg (2.1 mmol) CrO_3 in 1 ml (6 mmol) 6N HCl over a ten minute period. The resulting orange solid was collected on a sintered glass funnel by suction filtration. Recrystalization from boiling H_2O yielded a bright orange solid which was collected on a sintered glass funnel. The orange solid was dried under vacuum (10^{-3} torr) for 24

TABLE XV

X-RAY POWDER PATTERN OF $C_4H_5N_2OCrO_3Cl$

d(A)	Intensity	d(A)	Intensity
6.83	w	2.26	ms
6.15	ms	2.19	ms
5.61	mw	2.13	m
4.98	m	2.089	m
4.50	vs, br	2.020	mw
3.73	m	1.987	m
3.62	m	1.926	mw
3.40	ms	1.894	mw
3.21	w	1.840	w
3.15	s	1.815	ms
2.99	m	1.759	mw
2.70	ms	1.750	mw
2.53	m	1.708	mw
2.48	vw	1.676	m
2.43	m		
2.33	m		

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, br = broad

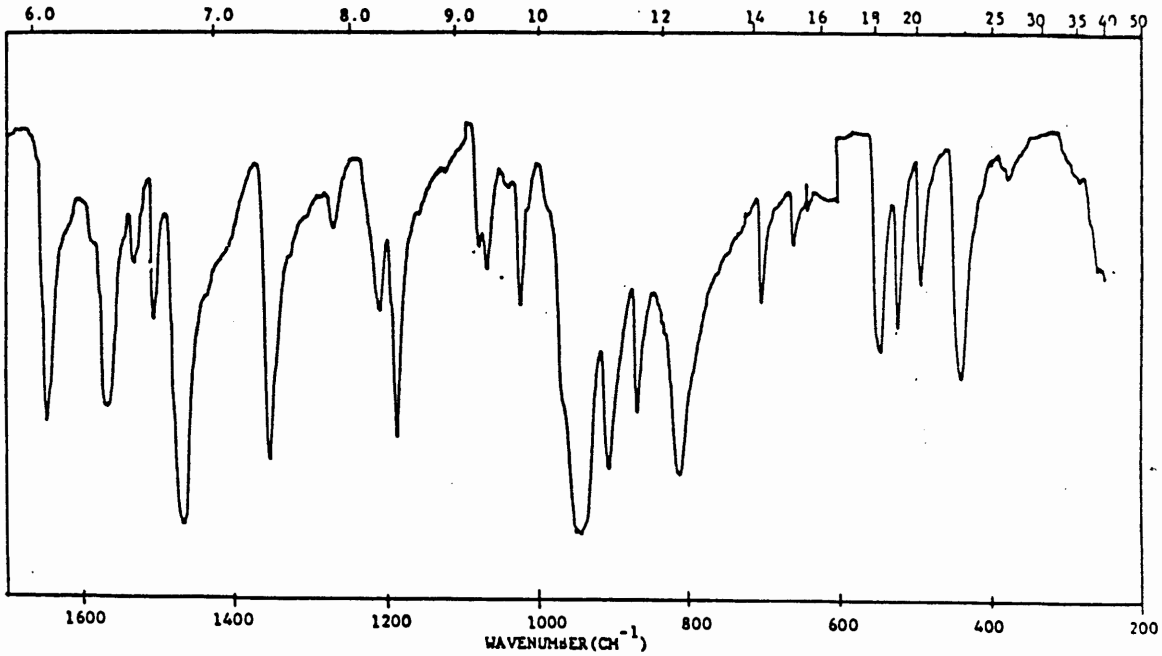


FIGURE 22. Infrared spectrum of $(C_4H_5N_2O)CrO_3Cl$

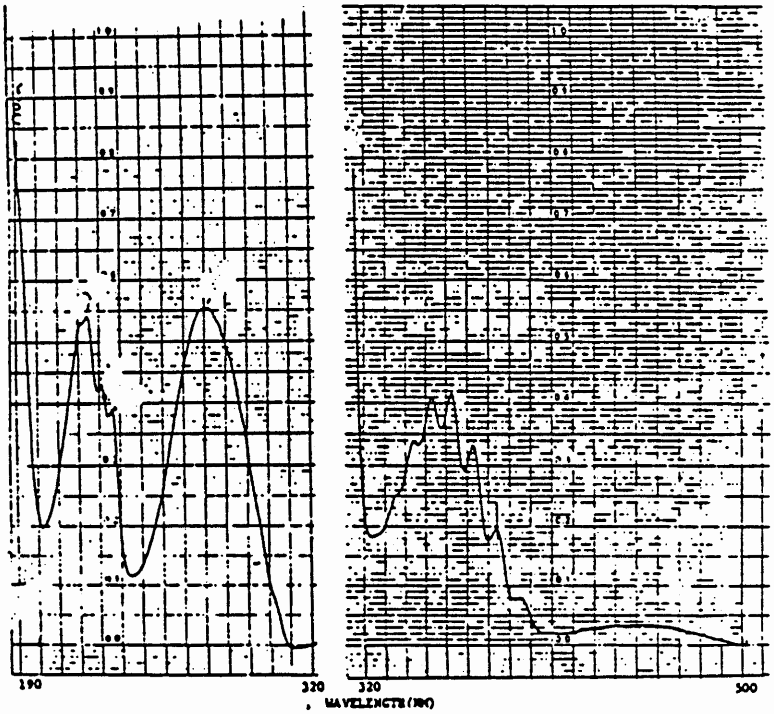


FIGURE 23. UV/VIS spectrum of $(C_4H_5N_2O)CrO_3Cl$

TABLE XVI

INFRARED SPECTRUM OF $(C_4H_5N_2O)CrO_3Cl$ IN CM^{-1}

$(C_4H_5N_2O)CrO_3Cl$	Assignment	$(C_4H_5N_2O)CrO_3Cl$	Assignment
3155 m	CH st	966 m, sh	ν_{as} Cr-O
3080 m, br	CH st	947 vs	ν_{as} Cr-O
3037 m, sh	CH st	939 vs	ν_{as} Cr-O
1644 m	ring	930 vs, sh	ν_{as} Cr-O
1563 m	ring	901 s	ν_{as} Cr-O
1528 w	ring	865 m	δ N-O
1503 mw	ring	808 s	CH def
1464 vs	CH be?	700 mw	CH def
1349 s	ν N-O ?	658 w	ring
1268 w		544 m	1563-1020=543
1207 mw	1644-437=1207	521 m	
1182 ms	ring	491 mw	
1076 w	ring or CH be	437 m	ν Cr-Cl
1065 mw	CH be		
1020 mw	ring or CH be		

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, br = broad, sh = shoulder, CH be = CH bend hrs. Yield, 0.72g (86.6%); m.p. 167-169°C dec. Analysis calculated for $C_{15}H_{13}N_3O_3Cl_2Cr$: C, 44.35, H, 3.23; N, 10.34; Cl, 17.46; Cr, 12.80. Found: C, 44.93; H, 3.06; N, 10.08; Cl, 17.08; Cr, 12.94.

The x-ray powder pattern is shown in Table XVII, and the infrared spectrum (1700 to $200cm^{-1}$) and the uv/vis spectrum are shown in Figures 24 and 25, respectively. The positions of the infrared absorptions are listed in Table XVIII. The complex is only very slightly soluble in CH_3CN and H_2O at room temperature, and insoluble in CH_2Cl_2, $(CH_3)_2CO$, and $(CH_3CH_2)_2O$. The complex is soluble in pyridine. The complex is nonhygroscopic, but stable for only one or two months when stored in the dark.

Reactions of Heterocyclic Systems with Chromium Trioxide in Non-acidic Aqueous and Non-aqueous Media.

When dissolved in water in the absence of acid, chromium trioxide forms the dichromate and bichromate ions:

IV-2 $2CrO_3 + H_2O \longrightarrow Cr_2O_7^{2-} + 2H^+$

IV-3 $CrO_3 + H_2O \longrightarrow HCrO_4^- + H^+$

The formation of these anions with the concomitant formation of H^+ causes the solution to become acidic, and between pH 2 and pH 6 an equilibrium is established between $Cr_2O_7^{2-}$ and $HCrO_4^-$ (70):

IV-4 $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad k = 10^{-2.2}$

The equilibrium is quite labile and on addition of cations

TABLE XVII

X-RAY POWDER PATTERN OF $(C_{15}H_{13}N_3Cl)CrO_3Cl$

d(A)	Intensity	d(A)	Intensity
7.44	w	3.34	m
6.68	ms	3.05	vs
6.19	vw	2.87	vw
5.60	ms, br	2.66	vw
5.00	ms, br	2.60	vw
4.45	w	2.41	w
4.19	m	2.35	w
3.93	ms	2.29	w
3.83	vs, br	2.24	w
3.59	vs	2.050	vw
3.46	w		

vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, br = broad

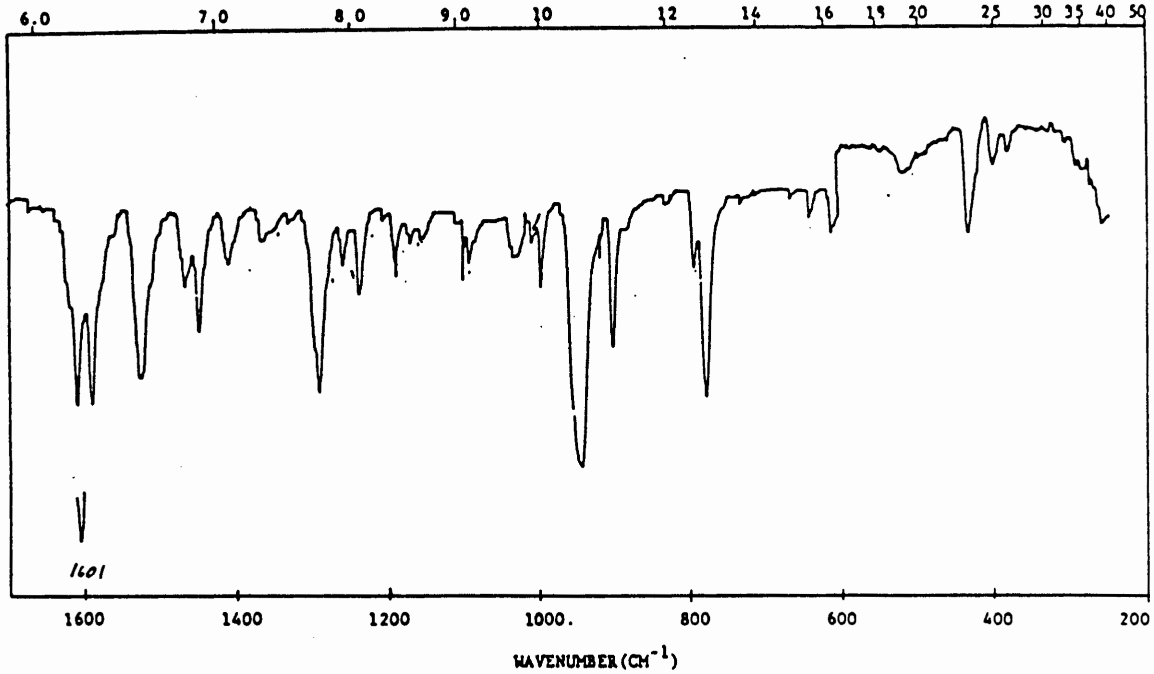


FIGURE 24. Infrared spectrum of $(C_{15}H_{13}N_3Cl)CrO_3Cl$

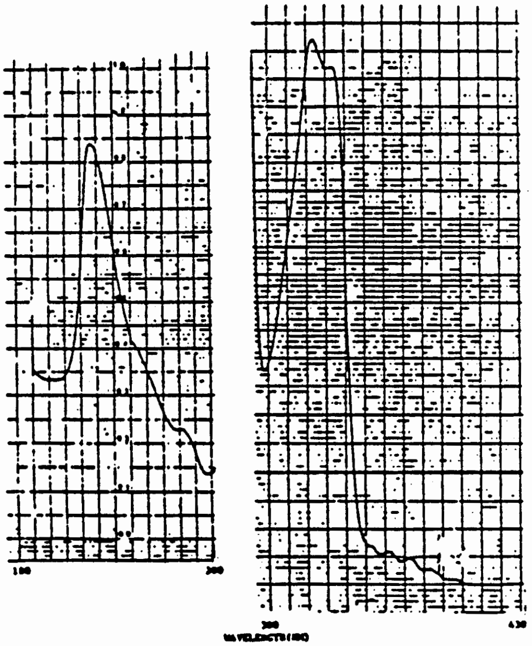


FIGURE 25. Uv/VIS spectrum of $(C_{15}H_{13}N_3Cl)CrO_3Cl$

TABLE XVIII

INFRARED SPECTRUM OF $(C_{15}H_{13}N_3Cl)CrO_3Cl$ IN CM^{-1}

3096	m
3050	w
2740	m, br
1607	s
1587	s
1523	s
1468	mw
1446	m
1408	mw
1363	w
1330	vw
1295	ms, sh
1288	s
1257	mw
1237	m
1206	vw
1188	w
1170	vw
1154	vw
1090	w
1029	w, br
1008	vw
996	mw
940	vs
899	m
881	vw
794	w
777	s
643	w
612	w
518	w
431	mw
399	w
380	w

s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, sh = shoulder, br = broad which form insoluble chromates (e.g. Ba^{2+}, Pb^{2+}, Ag^{+}) (71), the chromates and not the dichromates are precipitated. One would expect that addition of cations which form insoluble dichromates should result in the precipitation of the dichromate species exclusively.

In media in which chromium trioxide is insoluble (that is, when CrO_3 is in the solid state), CrO_3 exists as a long chain of corner sharing tetrahedra.

Reaction of Chromium Trioxide and Naphthyridine In Water. Naphthyridine, (0.788 mmol), was thoroughly dissolved in 1.5 ml H_2O and cooled to 0°C. A second solution containing 0.0827g (0.827 mmol) CrO_3 in 1 ml H_2O at room temperature was added dropwise to the naphthyridine solution. The formation of an orange solid product was slow, but became much more rapid after the initial crystals formed. The solution was allowed to stand at 0°C for 2 hours after which time the product was collected on a sintered glass funnel. The orange product was recrystallized twice from H_2O, yielding clean orange needle-like crystals which were dried under vacuum (10^{-3} torr) for five hours. Yield, 0.1116g (59.2%); m.p. 140-142 dec.. Elemental analysis calculated for $C_{16}H_{14}N_4O_7Cr_2$: C, 40.18; H, 2.95; N, 11.71; Cr, 21.74. Found: C, 40.74; H, 2.82; N, 11.81; Cr, 22.47.

The x-ray powder pattern is shown in Table XIX, and the infrared spectrum (1700 - 200cm^{-1}) and uv/vis spectrum

TABLE XIX

X-RAY POWDER PATTERN OF $(C_8H_6N_2H)_2Cr_2O_7$

d(A)	Intensity	d(A)	Intensity
9.64	w	1.851	w
8.59	w	1.826	w
7.59	w	1.802	mw
6.93	m	1.678	vw
6.44	vw	1.621	vw
5.53	w	1.580	vw
4.98	vs	1.539	vw
4.72	w	1.507	w
4.56	mw	1.491	w
4.24	s, br	1.462	vw
4.03	vw	1.439	vw
3.87	w		
3.64	mw		
3.47	s, br		
3.33	m		
3.28	vs		

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, br = broad

in H_2O (λ_{max} (nm); 357.6, 333.5, 324, 318.2, 281, 252.4, 226.1) are shown in Figures 26 and 27, respectively. The positions of the infrared absorptions and the vibrational mode associated with each is listed in Table XX. The complex is insoluble in CH_2Cl_2, $(CH_3CH_2)_2O$, CCl_4, and C_6H_6; slightly soluble in CH_3CN, $(CH_3)_2CO$, and soluble in pyridine.

Reaction of Pyrazine with Chromium Trioxide in Water. Pyrazine, (10.34 mmol), was thoroughly dissolved in 5.5 ml H_2O in a 25 ml round bottom flask equipped with a magnetic stir bar, and cooled to 0°C. A second solution containing 1.0029g (10.03 mmol) CrO_3 and 1 ml H_2O at room temperature was added dropwise to the pyrazine solution. After addition of approximately half of the CrO_3 solution, there was no solid present. Without further addition of the CrO_3 solution, the $C_4H_4N_2$ solution was stirred for five minutes at 0°C, after which time a large amount of solid formed. The remaining CrO_3 solution was then added dropwise, and the solution was stirred for 15 minutes at 0°C while being shielded from the light. The solution was then left at 0°C for one hour, and the deep orange crystals were collected on a sintered glass funnel. The solid was twice recrystallized from a minimum amount of H_2O yielding a deep red solid, which was dried under vacuum (10^{-3} torr) for 16 hours. Yield, 0.7175g (44.9%); m.p. 115.5°C dec. Elemental analysis calculated for $C_8H_{10}N_4Cr_3O_{10}$: C, 20.10; H, 2.11;

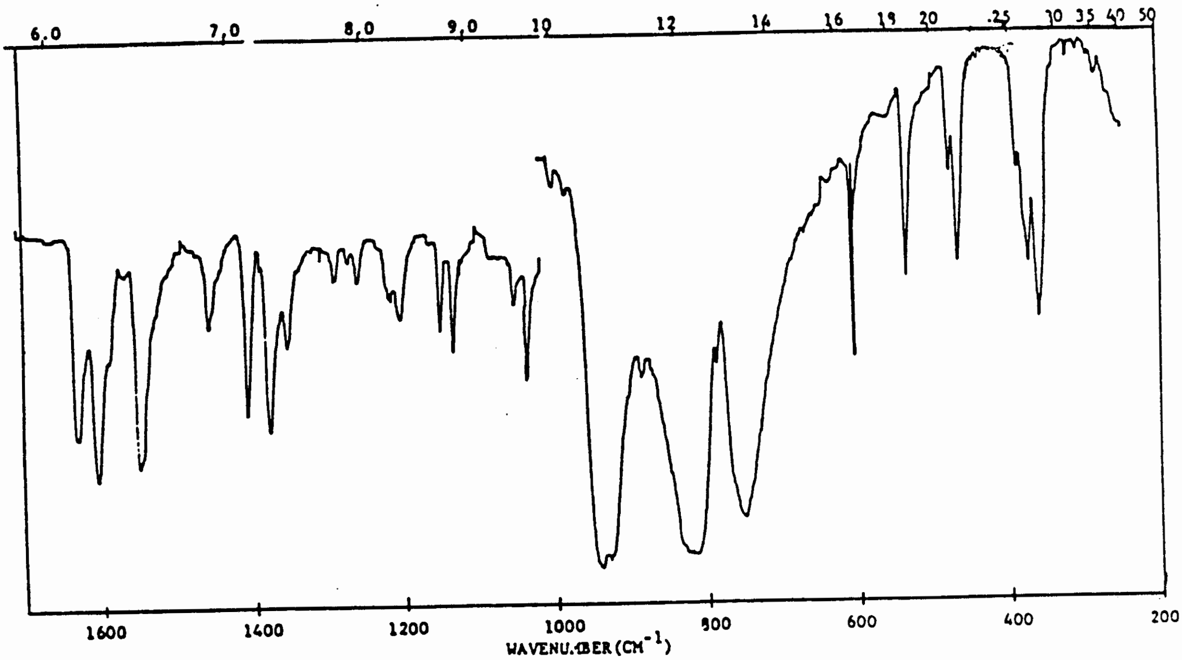


FIGURE 26. Infrared spectrum of $(C_8H_6N_2H)_2Cr_2O_7$

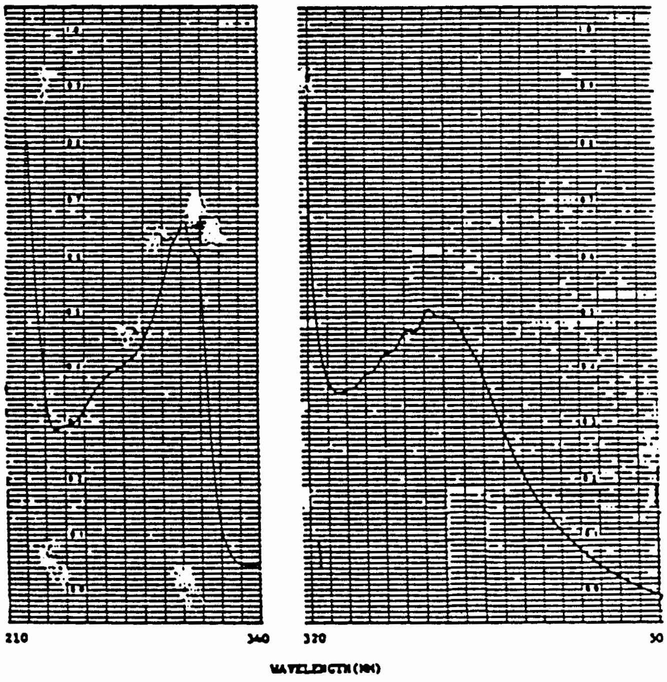


FIGURE 27. UV/VIS spectrum of $(C_8H_6N_2H)_2Cr_2O_7$

TABLE XX

INFRARED SPECTRUM OF $(C_8H_6N_2H)_2Cr_2O_7$ IN CM^{-1}

$(C_8H_6N_2H)_2Cr_2O_7$	Assignment	$(C_8H_6N_2H)_2Cr_2O_7$	Assignment
3100 mw	CH st	1048 w	1404-358=1046
3064 mw	CH st	1032 mw	sk st
3055 mw	CH st	1000 w	1373-370-1003
3020 w	CH st	938 vs	ν_{as} CrO_3
1625 ms	skel st	925 vs	ν_{as} CrO_3
1600 s	skel st	900 s, sh	ν_{as} CrO_3
1544 ms	skel st	883 s	ν_{as} CrO_3
1454 mw	skel st	818 vs, br	CH op be
1404 m	CH ip be	785 s, sh	ν_{as} CrOCr
1373 ms	skel st	751 vs	ν_{as} CrOCr
1350 m	skel st	603 m	
1286 w	CH ip be	533 m	ν_s CrOCr
1270 vw	CH ip be	477 w	
1257 w	CH ip be	466 m	
1199 m	?	387 m, sh	
1147 m	1625-477=1148	370 ms	δ CrO_3
1129 m	sk be	358 ms	δ CrO_3

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, vw = very weak, st = stretch, ip be = in plane bend

N, 11.71; Cr, 32.62. Found: C, 20.35, H, 2.13; N, 11.68; Cr, 33.19.

The infrared spectrum (1700 to 200cm^{-1}) and uv/vis spectrum (λ_{max} (nm) = 382.4, 294.6 (sh), 268.8, 262.7, 256.4 (sh)) are shown in Figures 28 and 29, respectively. The positions of the infrared absorptions and the vibrational modes associated with each are listed in Table XXI.

Reaction of Pyrazine with Chromium Trioxide in CH_2Cl_2 Under Dry Atmosphere Conditions. In a 50 ml round bottom flask equipped with a magnetic stir bar were placed 0.5057g (5.057 mmol) CrO_3 and 0.4994g (6.24 mmol) $C_4H_4N_2$. Dry CH_2Cl_2 (approximately 20 ml), was vacuum distilled into the round bottom flask, and one atmosphere of dry nitrogen was placed in the vessel. Upon removal from the vacuum line, a drying tube filled with indicator Drierite was immediately placed in the single neck 19/22 ground glass joint. The solution was allowed to warm to room temperature, yielding a clear yellow CH_2Cl_2 layer with the CrO_3 remaining undissolved. The reaction vessel was placed in a 0°C ice bath and stirring was initiated. After 15-20 minutes, the solution became cloudy, and within one hour there was obvious formation of a yellow solid; much undissolved CrO_3 remained at this point. After 3.75 hours all the CrO_3 appeared to have reacted, and the reaction vessel was tightly stoppered and sealed with Parafilm and cooled to -78°C overnight. While the solution was still cool, but

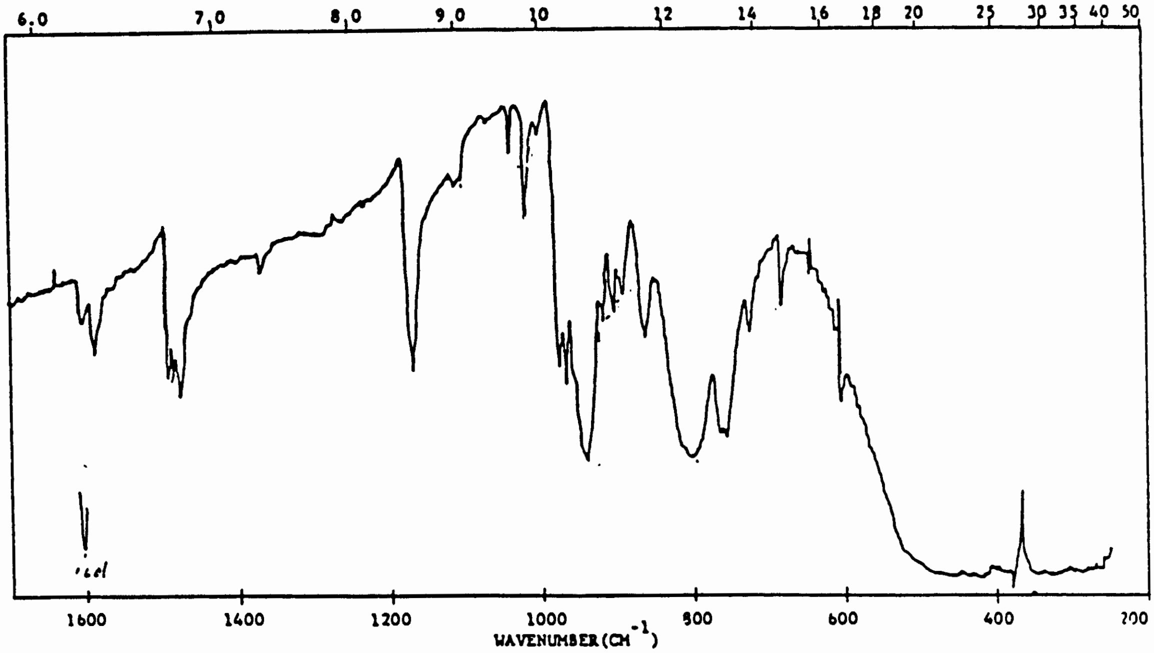


FIGURE 28. Infrared spectrum of $(C_4H_4N_2H)_2Cr_3O_{10}$

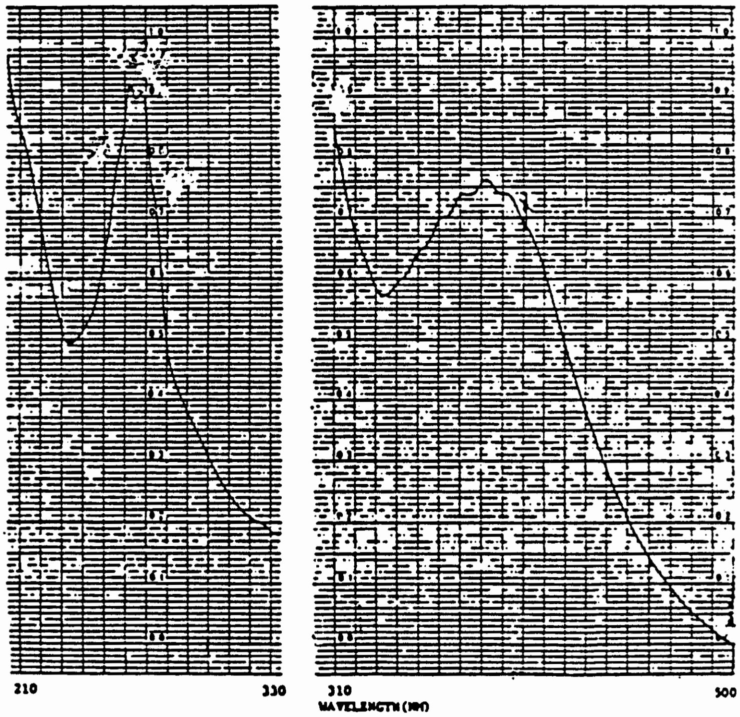


FIGURE 29. UV/VIS spectrum of $(C_4H_4N_2H)_2Cr_3O_{10}$

TABLE XXI

INFRARED SPECTRUM OF $(C_4H_5N_2)_2Cr_3O_{10}$ IN CM^{-1}

$(C_4H_5N_2)_2CrO_3O_{10}$	Assignment	$(C_4H_5N_2)_2CrO_3O_{10}$	Assignment
3128 mw	CH st	947 vs, sh	ν_{as} CrO_3
3058 mw	CH st	938 s	ν_{as} CrO_3
1601 w	ring	916 m	1482-563=919?
1586 mw	723+859=1582?	900 m	ν_s CrO_3
1488 m	ring	887 m	ν_s CrO_3
1482 m	372+1109=1481	859 ms	1586-723=863?
1472 mw	680+798=1478?	814 vs, sh	ν_{as} CrOCr
1367 mw	ring	798 s	CH
1168 ms	ring	761 s	CH
1109 w	CH be	754 ms	ν_{as} CrOCr
1037 w	CH be	723 m	
1017 mw	ring or CH be	650 m	1586-938=648
999 w	?	600 ms	
974 ms	ν_{as} CrO_2	563 mw	ν_s CrOCr
965 ms	ν_{as} CrO_2	515 mw	ν_s CrOCr
957 s, sh	ν_s CrO_2	407	
		372 ms	ring

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, sh = shoulder, st = stretch, be = bend the solid was rapidly filtered on a sintered glass funnel; the solid was immediately transferred to a 25 ml round bottom flask and placed under a vacuum (10^{-3} torr). As CH_2Cl_2 solvent was removed, the solid became a clean, bright yellow. Yield, 0.5027g (55.2%); m.p. > 350°C. Elemental analysis calculated for $C_4H_4N_2CrO_3$: C, 26.68; H, 2.24; N, 15.56; Cr, 28.87. Found C, 24.41; H, 2.14; N, 14.46; Cr, 30.24.

The x-ray powder pattern is shown in Table XXII, and the infrared spectrum (1700 - 200cm^{-1}) and the uv/vis spectrum (λ_{max} (nm) = 382.4, 267.6, 261.7, 255.4) are shown in Figures 30 and 31, respectively. The positions of the infrared absorptions and their respective assignments are listed in Table XXIII. The complex dissolves in H_2O and pyridine, is somewhat soluble in CH_3CN, and decomposes on standing in $(CH_3)_2O)$, CCl_4, and $CHCl_3$. The complex seems to be rather light-sensitive but moderately stable in air. When shielded from light it remains stable for months under a nitrogen atmosphere.

Discussion.

Formation of the Naphthyridinium Chlorochromate Complex (NapCC). Information obtained from infrared and ultraviolet/visible spectra support the formulation of the compound formed by the reaction of CrO_3, $C_8H_6N_2$, and HCl as composed of a monoprotonated naphthyridine ring forming the

TABLE XXII

X-RAY POWDER PATTERN OF $C_4H_4N_2CrO_3$

d(A)	Intensity	d(A)	Intensity
5.459	w	3.176	w
5.153	w	3.098	w
4.972	ms	2.883	vs
4.327	ms	2.792	w
4.144	ms	2.244	ms
3.193	vs	2.136	w
3.345	m		

vs = very strong, ms = medium strong, m = medium, w = weak

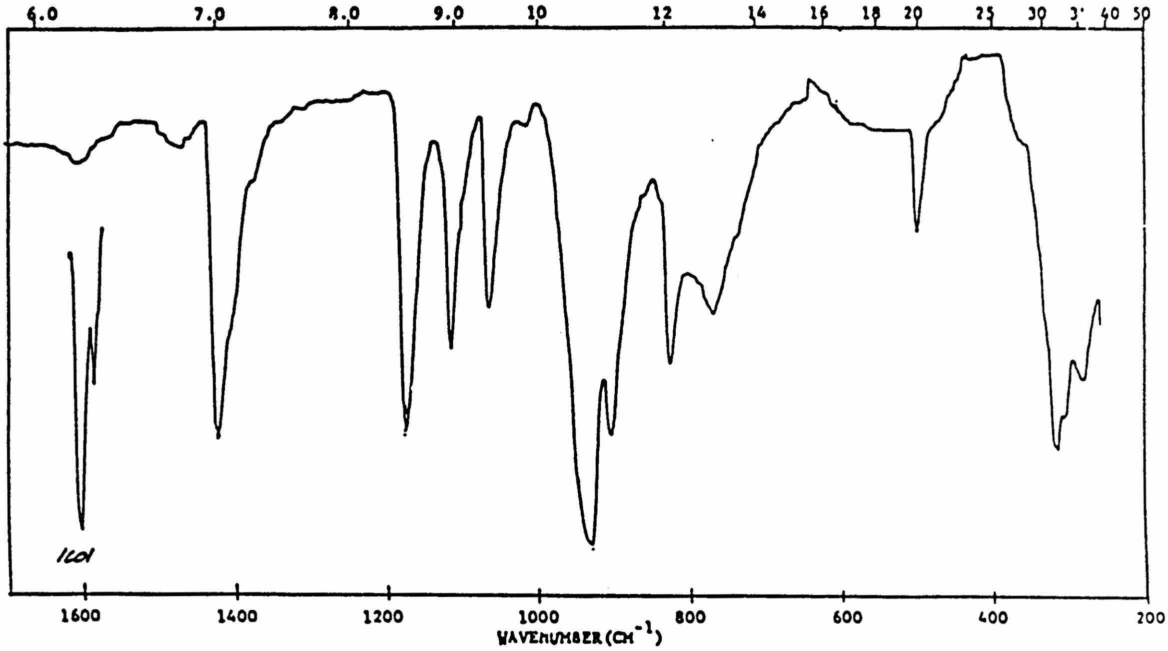


FIGURE 30. Infrared spectrum of $(C_4H_4N_2CrO_3)_n$

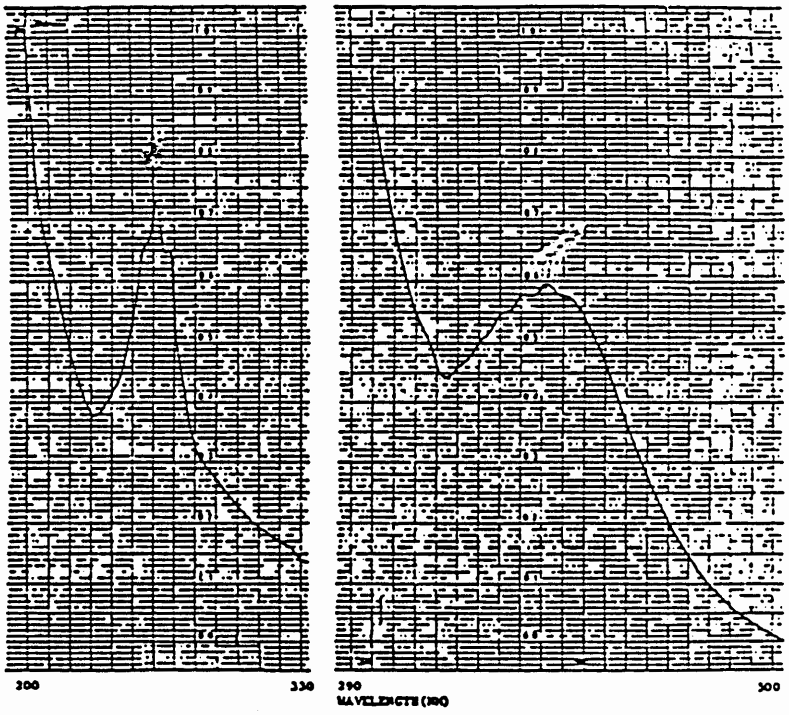


FIGURE 31. UV/VIS spectrum of $(C_4H_4N_2CrO_3)_n$

TABLE XXIII

INFRARED SPECTRUM OF $(C_4H_4N_2CrO_3)_n$

$(C_4H_4N_2CrO_3)_n$	Assignment	$(C_4H_4N_2CrO_3)_n$	Assignment
3095 m	CH st		
3042 m	CH st	928 vs	ν_{as} Cr-0
1422 s	ring?	902 s	ν_s Cr-0
1403 m	ring?	825 ms	CH
1372 w	312+1062=1374	767 m	CH
1172 s	ring	500 mw	ring
1114 ms	CH be	312 s	δ Cr-0
1062 m	CH be	302 s	δ Cr-0
1011 vw	ring or CH be	280 ms	ν Cr-N

vs = very strong, s = strong, ms = medium strong, m = medium, mw = medium weak, w = weak, st = stretch, be = bend cation, and the chlorochromate species forming the anion. Assuming an axially symmetrical tetrahedral configuration for the chlorochromate anion as has been found by x-ray diffraction measurements on solid $KCrO_3Cl$ (77), one would expect six fundamental vibrational modes in the infrared spectrum based on C_{3v} symmetry (78). Only three of these modes are readily assignable to CrO_3Cl^- in the infrared spectrum of NapCC; the others are either too weak or are not resolved. The infrared spectrum shows absorptions at 937 cm^{-1}, 898 cm^{-1}, and 419 cm^{-1} corresponding to ν_{asym} Cr=0, ν_{sym} Cr=0, and νCr-Cl, respectively. These are in accord with those found for $KCrO_3Cl$ (78).

In addition, the uv/vis spectrum shows absorptions typical for systems containing the CrO_3Cl^- anion (79); the spectrum shows a weak absorption at 450 nm in the visible region, and the edge of a very strong band at 300 nm, which extends further into the ultraviolet region. Of particular interest is an intense absorption centered at 359 nm which is itself divided into seven separate bands separated by 6.7nm; this fine structure has been attributed to a partially resolved vibrational progression due to excitation of a symmetric stretching mode in the CrO_3 group (79). The broad, strong absorption at 359 nm results from a charge transfer from oxygen to a d orbital on chromium.

Further evidence for the ionic character of this complex can be obtained from a comparison of the uv/vis spectrum of $(C_8H_6N_2H)CrO_3Cl$ around 300 nm and the uv/vis spectrum of the protonated naphthyridine, prepared by dissolving naphthyridine in CH_3CN and bubbling HCl through the solution for 15-20 minutes; the uv/vis spectrum of the protonated naphthyridine is shown in Figure 32. The two spectra are virtually superimposable in this region with absorptions at 302 and 309 nm. The complex is shown in Figure 36.

Formation of the Pyrazinium Chlorochromate Complex (PzCC). The infrared and uv/vis spectra both strongly agree with the formulation of this complex as containing the chlorochromate anion. The infrared spectrum shows absorptions at 938, 901, and 423 cm^{-1} which can be assigned to the antisymmetric ν Cr=O, symmetric ν Cr=O, and ν Cr-Cl stretching modes, respectively; these are in strong agreement with those found for naphthyridinium chlorochromate and $KCrO_3Cl$ for the chlorochromate anion. The uv/vis spectrum also strongly agrees with the spectrum found for NapCC in which the chlorochromate anion is postulated. To confirm the ionic character of PzCC, the uv spectrum of PzCC was compared to the spectrum of the protonated pyrazine, prepared as for the protonated naphthyridine, and shown in Figure 33b. In the pyrazine case, however, the spectrum of PzCC in the 250-270 nm region strongly resembles the spectrum of the unprotonated form shown in Figure 33a. The observation that pyrazine exists in a nonprotonated form

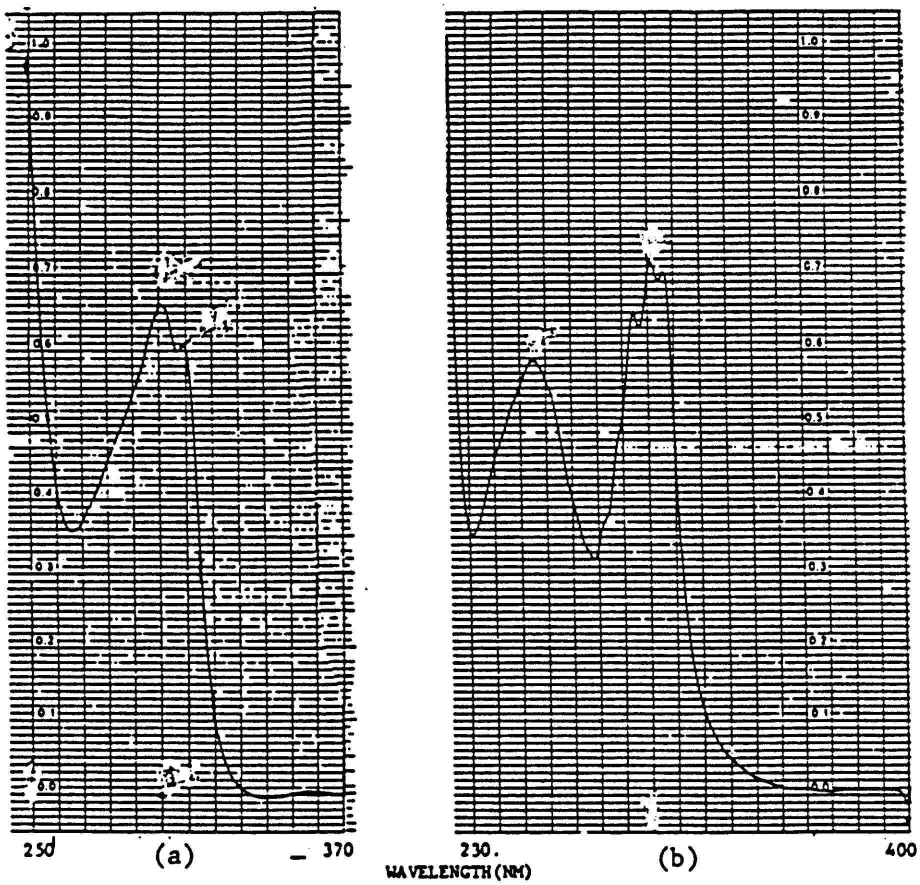


FIGURE 32. UV/VIS spectra of $(C_8H_7N_2)^+$ (a), and $C_8H_6N_2$ (b) in CH_3CN

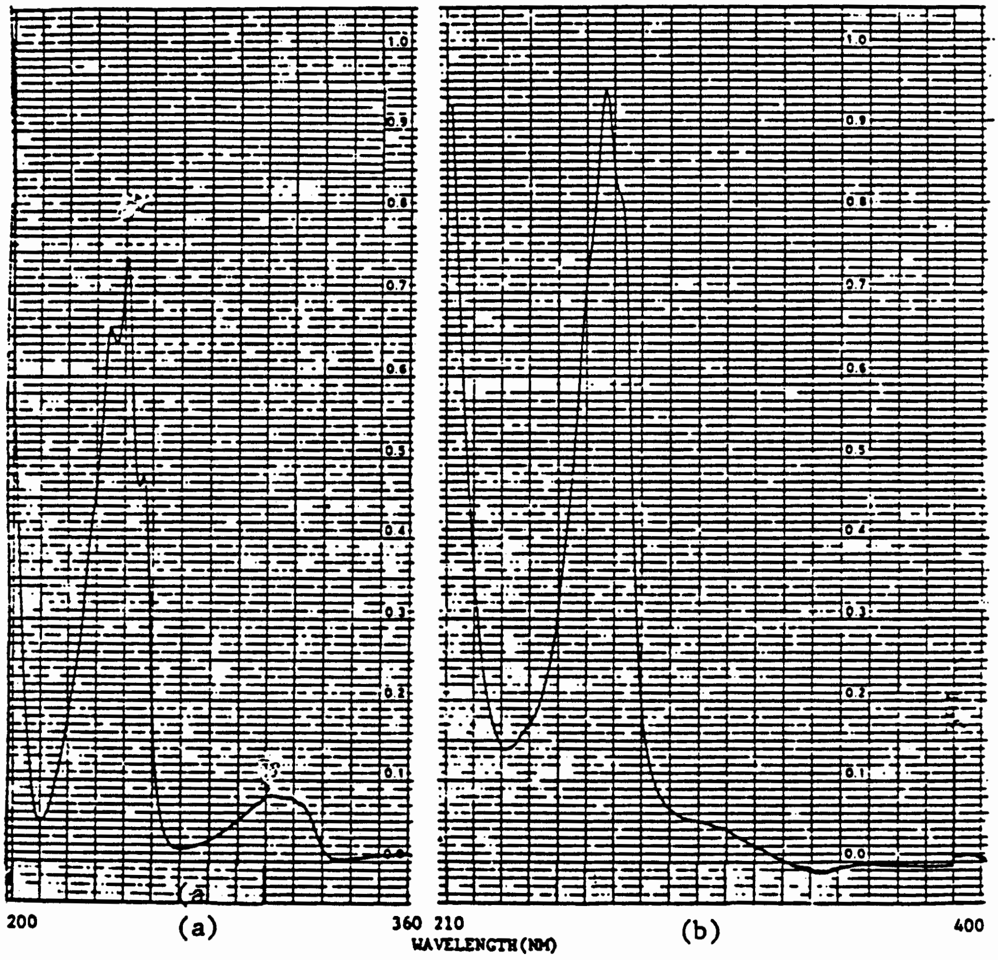


FIGURE 33. UV/VIS spectra of $C_4H_4N_2$ (a)~~,~~ and $(C_4H_4N_2H)^+$ (b) in CH_3CN

when PzCC is dissolved in solution is due to the low pk_a of pyrazine (pk_a = 0.95); thus, upon dissolving in CH_3CN, free pyrazine is liberated. The low pk_a of pyrazine also accounts for the observation that pyrazine is readily displaced as the cation by pyridine, (pk_a = 5.35). The complex is shown in Figure 36.

Formation of Pyrazinium-N-oxide Chlorochromate. The well-resolved spectral region between $900cm^{-1}$ and $1000cm^{-1}$ in the infrared spectrum of this complex shows absorptions at $966cm^{-1}$, $947cm^{-1}$, $939cm^{-1}$, and $930cm^{-1}$ which strongly agree with the antisymmetric Cr=0 stretching modes for the chlorochromate anion; also found are absorptions at $901cm^{-1}$ and $437cm^{-1}$, corresponding to the symmetric νCr=0 and ν Cr-Cl vibrational modes, respectively for the chlorochromate group. The uv/vis spectrum confirms the infrared interpretation in indicating the chlorochromate group; the broad absorption centered at 360 nm with seven peaks, each separated by 7.2 nm, superimposed on this peak is typical of the chlorochromate anion.

Of special interest in the infrared spectrum are the absorptions at $1349cm^{-1}$ and $865cm^{-1}$ corresponding to ν N-0 and δ N-0, respectively (66). These absorptions are shifted to higher frequencies relative to the free pyrazine-N-oxide where ν N-0 and δ N-0 are located at $1340cm^{-1}$ and $860cm^{-1}$, respectively. A positive shift, such as this, has been interpreted as being due to the drain in electron density from the coordinated atom to the metal center in neutral complexes. This leads to an increase in the contribution of the N-0 oxygen orbitals to the system of the aromatic ring, and hence strengthens the N-0 bond (80). Thus, a positive shift in the ν N-0 and δ N-0 frequencies is thought to indicate coordination of pyrazine-N-oxide through the unoxidized nitrogen rather than through the N-0 oxygen. If one then considers that the effect of a proton located on the unoxidized nitrogen atom, in causing a slight drain of electron density from the nitrogen atom, will be similar to the case for metal coordination, then the positive shifts observed for νN-0 and δ N-0 in the infrared suggest that the unoxidized nitrogen is the site of protonation in the chlorochromate complex. This is in agreement with several studies which report that the unoxidized nitrogen in pyrazine-N-oxide is the initial site of protonation (81). Further protonation of the N-0 oxygen was found to be quite slow. The proposed structure of the pyrazinium-N-oxide chlorochromate complex is shown in Figure 36.

One anomaly in the uv spectrum of the chlorochromate complex in the 200-300 nm region is that it does not match that of the protonated pyrazine-N-oxide (prepared analogously to the protonated pyrazine) shown in Figure 34b, (λmax = 286.6), or that of the non-protonated pyrazine-N-oxide shown in Figure (34a), (λmax = 272 nm, 220 nm). The reason for this anomaly is not obvious. One

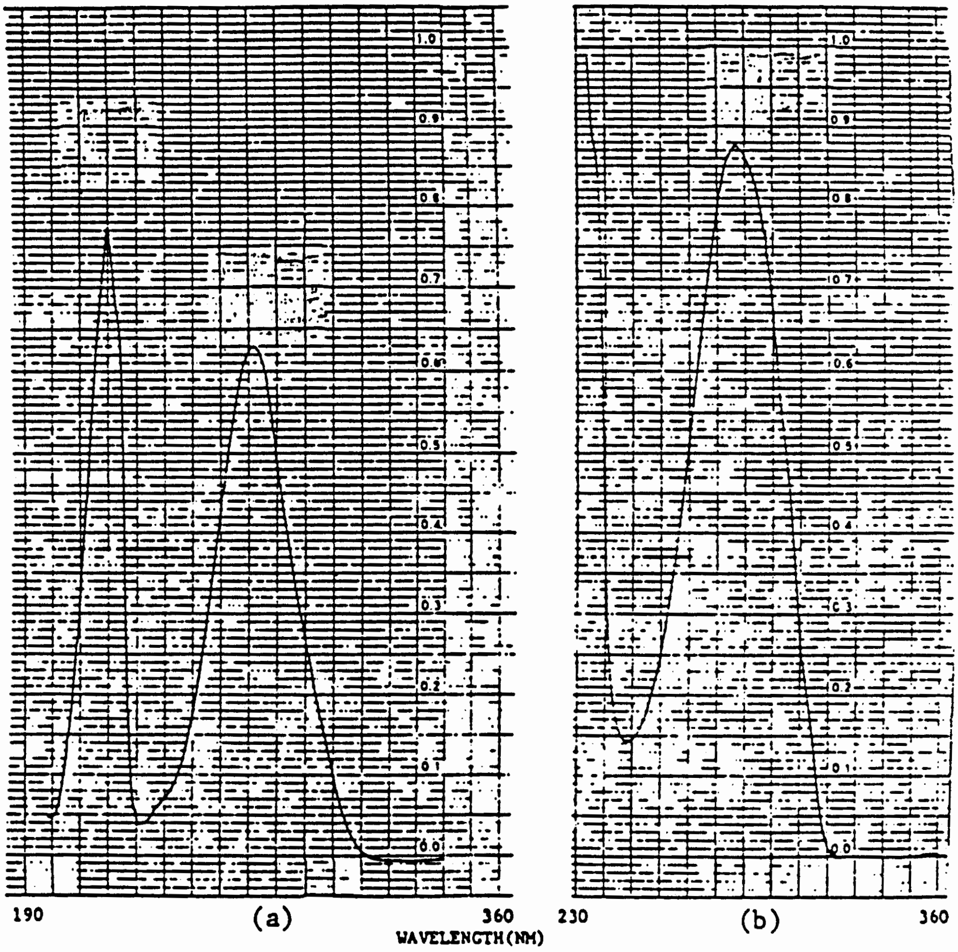


FIGURE 34. UV/VIS spectra of $C_4H_4N_2O$ (a), and $(C_4H_4N_2OH)^+$ (b) in CH_3CN

explanation is that there could be direct coordination of pyrazine-N-oxide through the unoxidized nitrogen atom to the metal center as has been found for some chlorochromate complexes of aliphatic amines and pyridine (82), but this possibility is precluded by infrared evidence which shows that the C_{3v} symmetry of the CrO_3Cl group has been preserved, and the absence of any absorptions assignable to νCr-N modes.

Formation of Tripyridinium-hydrochloride Chlorochromate. The infrared absorptions at $940cm^{-1}$ and $899cm^{-1}$ for this complex can be unambiguously assigned to the antisymmetric νCr=0 and symmetrical νCr=0, respectively of the chlorochromate group; the absorption at $431cm^{-1}$ corresponds to the νCr-Cl stretching mode of the chlorochromate group. The uv spectrum shows a broad absorption centered at 357.6 nm, which, although partially overlapped by an intense uv absorption due to the protonated tripyridine, shows the fine structure associated with the chlorochromate anion.

Tripyridine has three nitrogen atoms with free lone pairs of electrons, and thus has three potential sites for protonation. Due to the presence of the chlorochromate anion, protonation at one nitrogen is assumed in order to produce a cation. Based on the elemental analysis there is also one molecule of HCl associated with the tripyridinium complex. A broad absorption at $2740cm^{-1}$ can be assigned to

ν NH-Cl stretching mode, similar to that found for pyridine hydrochloride (83), and thus suggests that the tripyridine ring system is diprotonated with chlorochromate and chloride acting as anions. The proposed structure of tripyridinium-hydrochloride chlorochromate is shown in Figure 36.

Formation of bis-Naphthyridinium Dichromate. The infrared spectrum shows absorptions at 785cm^{-1}, 751cm^{-1}, and 533cm^{-1} for this complex, which can be unambiguously assigned to Cr-O-Cr bridging stretches (84). This clearly indicates that the crystal structure consists of a di- or poly-chromate group. The infrared spectrum in the 880cm^{-1} to 950cm^{-1} region (ν Cr=O region) resembles quite closely the spectrum of $(NH_4)_2Cr_2O_7$ (84), and on this basis the product is formulated as $(C_8H_6N_2H)_2Cr_2O_7$. This is also a reasonable formulation based on the method of synthesis since Cr(VI) exists primarily as $Cr_2O_7^{2-}$ in an aqueous solution under the reaction conditions employed in the formation of the complex. Corey and Schmidt prepared bis-pyridinium dichromate in a similar manner (33).

The uv/vis spectrum of the complex also supports the conclusion that dichromate forms the anion in this complex. The spectrum between 310 nm and 400 nm very closely resembles that reported for $Cr_2O_7^{2-}$ (85). The charge transfer band centered at 382.4 nm shows fine structure which has been interpreted as arising from transitions from the ground level to various overtones of a vibrational level associated with an excited electronic level. A second broad absorption at 274.7 nm characteristic of a O_3CrO molecular arrangement is partially overlapped by absorptions of the naphthyridine ring system. The absorptions observed at 307.9 nm and 301.2 nm for the dichromate complex compare favorably with those found for the protonated naphthyridine (309 nm and 301.2 nm). Thus the uv/vis spectral evidence agrees well with the infrared evidence in support of the formulation as $(C_8H_6N_2H)_2Cr_2O_7$ for this complex; the complex is shown in Figure 36.

Formation of the bis-Pyrazinium Trichromate Complex. The infrared spectrum of this complex shows absorptions at 814cm^{-1}, 754cm^{-1}, 563cm^{-1}, and 515cm^{-1} which can be attributed to Cr-O-Cr stretching vibrations (84), and the 900cm^{-1} to 1000cm^{-1} region shows absorptions which can be assigned with certainty to terminal Cr=O stretches. This indicates that the complex is composed of a di- or polychromate species. Since chromium trioxide dissolves in water to yield primarily $Cr_2O_7^{2-}$ under the reaction conditions employed, it is reasonable to assume that the product may contain a di-or polychromate anion. Based on the equilibrium of dichromate and chromate ions, a chromate species could conceivably have been formed; but infrared evidence rules out this possibility. Upon close examination of the infrared spectrum between 880cm^{-1} and 990cm^{-1}, one can identify eight absorptions; the spectrum of $K_2Cr_2O_7$ shows eleven absorptions in this region, while $Cs_2Cr_3O_{10}$ shows only six absorptions. A comparison of the infrared spectrum of the new pyrazinium complex to that of $Cs_2Cr_3O_{10}$ (86) shown in Table XXIV shows very strong similarities. The formation of a trichromate species is plausible based on the reaction:

IV-5 $2\ C_4H_4N_2 + 2\ CrO_3 + H_2O \longrightarrow (C_4H_4N_2H)_2Cr_2O_7$

$(C_4H_4N_2H)_2Cr_2O_7 + CrO_3 \longrightarrow (C_4H_4N_2H)_2Cr_3O_{10}$

This same reaction scheme was employed in the preparation of $Rb_2Cr_3O_{10}$, which crystallizes out of a H_2O solution as dark red prismatic crystals (87). Alternatively one could consider the reaction to be:

IV-6 $3(C_4H_5N_2)_2Cr_2O_7 \longrightarrow 2(C_4H_5N_2)_2Cr_3O_{10} + 2C_4H_4N_2 + H_2O$

The free pyrazine could have been removed either by remaining in the filtrate, or by sublimation under vacuum during the drying process; similar reasoning was employed to explain the formation of $((hfac)_2Cu)_2C_4H_4N_2$ from $Cu(hfac)_2(C_4H_4N_2)_2$ (88).

The uv/vis spectrum provides no distinction between $Cr_2O_7^{2-}$ and $Cr_3O_{10}^{2-}$, but this is to be expected since in each case each chromium center is surrounded by a distorted tetrahedran of oxygen atoms. Therefore, just as gives the same uv spectrum as does CrO_4^{2-} (85), $Cr_3O_{10}^{2-}$ can be expected to give the same uv spectrum as $Cr_2O_7^{2-}$ since the trichromate ion is itself composed of three CrO_4

TABLE XXIV

INFRARED SPECTRA OF $Cs_2Cr_3O_{10}$ AND $(C_4H_4N_2H)_2Cr_3O_{10}$ BETWEEN 880 AND 990CM^{-1}

$Cs_2Cr_3O_{10}$	$(C_4H_4N_2H)_2Cr_3O_{10}$	Assignment
976 s	974 ms	$\nu_{as}CrO_2$
963 s, sh	965 ms	$\nu_{as}CrO_2$
955 vs	956s, sh	$\nu_{s}CrO_2$
948 vs, sh	947 vs, sh	$\nu_{as}CrO_3$
934 s	938 s	$\nu_{as}CrO_3$
	916 m	
903 m	900 m	$\nu_{s}CrO_3$

vs = very strong, s = strong, ms = medium strong, m = medium, sh = shoulder tetrahedra joined by shared corners (30). The proposed structure of the product is shown in Figure 36.

Formation of $C_4H_4N_2CrO_3$. The infrared absorptions at 928cm^{-1} and 902cm^{-1} can be assigned to ν_{as} and ν_s Cr-0, respectively. There are, however, no absorptions attributable to ν Cr-0-Cr vibrations, and hence an oxygen-bridged structure can be ruled out. The assignment of the absorptions between 280cm^{-1} and 312cm^{-1} as νCr-N vibrations is similar to assignments made for the $MoOCl_3C_4H_4N_2$ complex (65a), as well as the assignment of the 290 - 295cm^{-1} infrared absorptions in various Etard complexes to νCr-N vibrational modes (89). It is also probable that the 302cm^{-1} and 312cm^{-1} bands are caused by δ Cr-0 vibrations.

The high melting point and the low solubility in most solvents suggests that the complex may be highly polymerized. Since an oxygen-bridged structure is precluded by the infrared evidence, the bridging would have to occur through the pyrazine, with pyrazine acting as a bridging bidentate ligand. The bidentate bridging nature of pyrazine in bimetallic and polymeric complexes is well known (65b, 90, 32). In general, the infrared spectra of complexes where pyrazine acts as a bridging bidentate ligand are simpler than those where pyrazine bonds in an unidentate fashion. This is thought to arise from a lowering of the symmetry of pyrazine in going from bridging bidentate to unidentate coordination, D_{2h} to C_{2v}, respectively (65c, 88, 31). Representative spectra of unidentate and bridging bidentate coordination modes are shown in Figure 35 for $SnBr_4(C_4H_4N_2)_2$ and $SnBr_4C_4H_4N_2$, respectively (88). Comparison of the infrared absorptions due to pyrazine in the spectrum of the $CrO_3C_4H_4N_2$ complex with that of $SnBr_4C_4H_4N_2$, which has been postulated as a polymer, shows the two spectra to be substantially similar.

This, taken with the occurrence of an infrared absorption in the Cr-N stretching region, and the absence of any absorptions assignable to νCr-0-Cr vibrations, indicates a polymeric structure for the $CrO_3C_4H_4N_2$ complex, with bridging bidentate pyrazine. The proposed complex is shown in Figure 36.

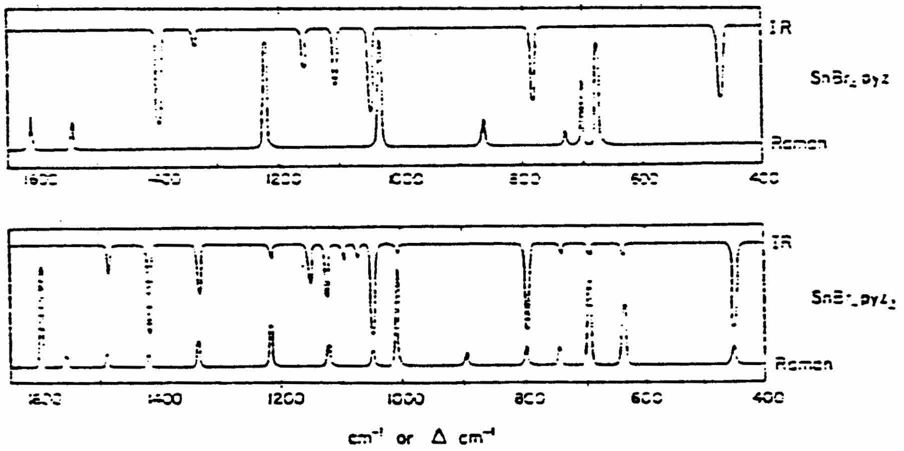


FIGURE 35. Infrared spectra of bridging bidentate and unidentate coordination of pyrazine in $SnBr_4C_4H_4N_2$ and $SnBr_4(C_4H_4N_2)_2$, respectively

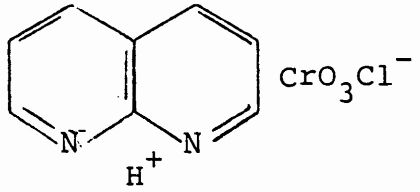
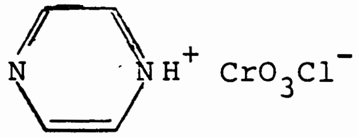
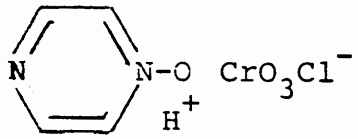
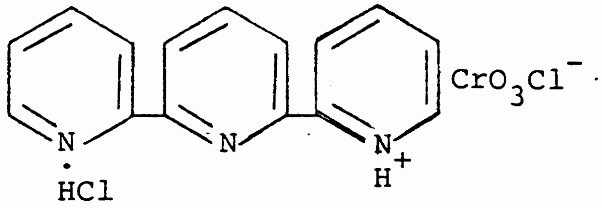
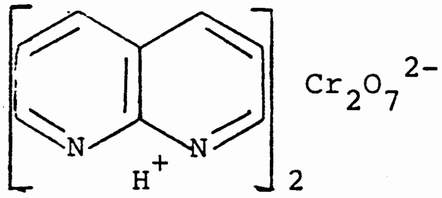
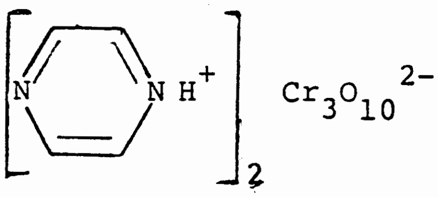
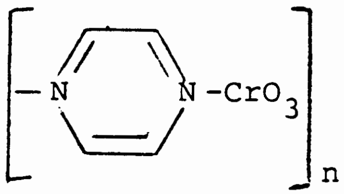
Proposed Structure	Name of Complex
	Naphthyridinium chlorochromate
	Pyrazinium chlorochromate
	Pyrazinium-N-oxide chlorochromate
	Tripyridinium-hydrochloride chlorochromate
	Naphthyridinium dichromate
	Pyrazinium trichromate
	Pyrazine chromium(VI) oxide

FIGURE 36. Proposed Structures of New Chromium(VI) Complexes.

CHAPTER V

OXIDATION OF ALCOHOLS BY NEW Cr(VI) HETEROCYCLIC COMPLEXES

Introduction

Recent progress in synthetic organic chemistry has led to the synthesis of some very elaborate molecules which contain one or more functional groups, or which have been derived from multifunctional starting materials. Many of these products are obtained through multistep synthetic routes where percent yield and possible by-product contamination are important considerations. To satisfy conditions for clean processes with high yields, highly selective reagents are required. A current interest in such reagents centers around chemoselective oxidation reagents; that is, oxidizing agents which are able to discriminate among more than one functional site in a molecule without resorting to special activating or blocking groups (91).

Studies of the oxidizing ability of hexavalent chromium complexes for the purpose of converting alcohols to carbonyl compounds has recently received considerable attention in the literature (24, 33, 34, 35, 92). Hexavalent chromium complexes have also been used successfully for the allylic oxidation of olefins (93), and for the oxidation of the carbon-carbon double bond of olefins, yielding carbonyl compounds or polymers (94).

The reduction potential of Cr(Vl) makes it especially suitable as an oxidizing agent:

V-1 $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr(III) + 7H_2O$ 1.33v

and

V-2 $HCrO_4^- + 7H^+ + 3e^- \longrightarrow Cr(III) + 4H_2O$ 1.195v

Thus the dichromate and bichromate ions are powerful oxidizing agents. They are however considerably weaker than the permanganate ion:

V-3 $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$ 1.68v

but are considerably stronger than the hypochlorite ion:

V-4 $ClO^- + H_2O + 2e^- \longrightarrow Cl^- + OH^-$ 0.90v

Thus Cr(Vl) has the advantage of being a strongly oxidizing reagent, but not so strong as to cause immediate oxidation of primary and secondary alcohols to carboxylic acids as occurs with MnO_4^-. However, the reduction potential of the metal cation only imparts a thermodynamic effect on the reaction, and equally important kinetic effects, such as the energy of activation or the lifetime of an excited state or intermediate metal substrate complex play a major role in oxidation reactions.

The mechanism for the oxidation of alcohols by Cr(VI) in an aqueous solution has been fairly well elucidated insofar as the first step proceeding through the chromic acid ester of the alcohol (95):

V-5 $R_2CHOH + HCrO_4^- + H^+ \longrightarrow R_2CHOCrO_3H + H_2O$

The carbon atom taking part in the ester linkage must then lose a proton to form the carbonyl compound, H_3O^+, and $HCrO_3^-$. However, kinetic studies (10, 96) show that while some three electron oxidations proceed through a 1:1 Cr(VI): substrate complex, most common examples proceed through a 1:2 Cr(VI): substrate complex (96d). These kinetic studies were designed so as to be able to observe the long postulated Cr(V) intermediate in the oxidation mechanism, and a proposed mechanism based on these studies is (96d):

V-6 $A + B + Cr(VI) \longrightarrow A - Cr^{VI} - B$

V-7 $A - Cr^{VI} - B \longrightarrow C + Cr(III) + \cdot R$

V-8 $\cdot R + Cr(VI) \longrightarrow D + Cr(V)$

V-9 $A + Cr(V) \longrightarrow C' + Cr(III)$

V-10 $B + Cr(V) \longrightarrow D' + Cr\ (III)$

A possible fault with these studies, and all the others which attempt to prove the existence of a Cr(V) intermediate, is that one of the species, A or B, must be an organic acid; this is necessary in order to stabilize the Cr(V) intermediate long enough for detection by either esr or uv/vis spectroscopic techniques. So currently there is strong evidence for a Cr(V) intermediate in Cr(VI) oxidations, but this so far hasn't been proven for the case where only an alcohol is present.

One of the disadvantages in the use of chromic acid as an oxidizing agent, for which the previous discussion on mechanistic studies is applicable, is that is is so strongly oxidizing that it has very low, if any degree of selectivity. It would for example be difficult to selectively oxidize an alcohol containing another easily oxidizable group such as a carbon-carbon double bond, a sulfide linkage, or a phenolic or amine group. Another disadvantage is the possibility of carbon-carbon bond cleavage in 2° and 3° alcohols (96d). Furthermore, the aldehyde produced from the oxidation of a 1° alcohol is itself easily oxidized to the acid by H_2CrO_4.

Modifications in using H_2CrO_4 include using acetone solutions of the alcohol in conjunction with a dilute sulphuric acid solution of H_2CrO_4, and using acetic acid as the solvent rather than water. These modifications result in non-alcohol functions not being oxidized, but provide no higher degree of selectivity between alcohol functions (i.e. 1°, 2°, 3°, benzylic, etc...).

It has also been shown that the rate of oxidation by chromic acid in aqueous solutions is diminished by the addition of chloride ion (97). The effect of chloride ion is not due to its basicity, or to oxidation of chloride to hypochlorite (95a), but rather has been explained on the assumption that the chlorochromate ion formed is a poor oxidizing agent compared to chromic acid.

It is interesting to consider why this should be the case. In a simplified reaction scheme, the oxidation of an alcohol by $HCrO_3Cl$ in H_2O can be represented by the following equilibria (95a):

V-11 $ClCrO_3^- + H_3O^+ \rightleftharpoons ClCrO_3H + H_2O$

V-12 $ClCrO_3H + ROH \rightleftharpoons ROCrO_2Cl + H_2O$

V-13 $ROCrO_2Cl + H_2O \rightleftharpoons RC{=}O + CrO_2Cl^- + H_3O^+$

Since the esterification reaction 12 is thought to occur through the undissociated chlorochromic acid, a shift to the left or right in the equilibrium reaction 11 will have a substantial effect on reaction 12. Because $ClCrO_3H$ is a stronger acid than H_2CrO_4 (98), the equilibrium 11 will be shifted further to the left for $HCrO_3Cl$ than H_2CrO_4, and thus the equilibrium 12 will be shifted to the left; that is, to the nonesterified reactants. The result is that there will be a lower concentration of the chromate ester for the oxidation process 13. But unlike reaction 11, reaction 13 will be favored by the stronger acid $HCrO_3Cl$ than H_2CrO_4 in high dielectric solvents. From these considerations it can be seen that reactions 11 and 13 compete against each other, and the deciding factor in determining the oxidizing ability of either chromate species will depend on which reaction "wins out." As it turns out, the Cr-Cl dipole is closer to the ionizable proton of the acid than to the proton lost from the chromate ester (95a, 99), thus the more polar chromate ester will be somewhat more stabilized in a high dielectric solvent than $HCrO_3Cl$; this causes the $HCrO_3Cl$ to dissociate more readily into its ions than the chlorochromate ester. Thus the shift of the equilibrium in 11 to the left is favored over the shift to the right of the equilibrium in 13. For H_2CrO_4 the situation will be reversed due to further shifts to the right for both 11 and 13; thus H_2CrO_4 is a stronger oxidizer than $HCrO_3Cl$ in high dielectric solvents.

As the medium is changed from a high dielectric solvent such as H_2O, to a low dielectric solvent, the reaction equilibria will be changed considerably. Reaction 11 will be shifted to the right for both $HCrO_3Cl$ and H_2CrO_4; in 85% acetic acid for example, there is little or no undissociated H_2CrO_4 (100), and one can conclude that the situation will be similar for $HCrO_3Cl$. However, in such solvents the decomposition reaction 13 will be particularly unfavorable due to the formation of ions. Therefore any shift to the right for 13 will be dependent on the stability, or instability of the chromate ester. In this case, the electrostatic considerations that were unfavorable for the decomposition of the chlorochromate ester in a high dielectric solvent will be favorable for a low dielectric solvent, and chlorochromate should be a good oxidizing agent under such conditions.

Several chlorochromate complexes have been studied as oxidizing agents in nonaqueous, low dielectric solvents. The use of low dielectric solvents not only enhances the oxidizing ability of the chlorochromate complex, but it also allows for the easy separation of the final organic product due to the insolubility of the chromium species. The complexes which have been studied include the well known pyridinium chlorochromate (32), bipyridinium chlorochromate (34), and 4-(dimethylamino)pyridinium chlorochromate (35) complexes; all of these complexes are effective in oxidizing alcohols to carbonyl compounds. The use of various organic cations causes the chlorochromate complex to become a milder oxidant, and in some cases increases its selectivity.

Hexavalent chromium, as potassium or sodium dichromate, is commonly used as an oxidizing agent in organic syntheses. Being a very strong oxidizing agent, like H_2CrO_4, it shows very little, if any, degree of selectivity. Unlike the case for the chlorochromate anion where its oxidizing ability has been decreased by the use of organic cations, few examples of organo dichromate complexes are to be found in the literature. One of the few examples is the pyridinium dichromate (PDC) complex. The early reports of oxidations employing this reagent involved the <u>in situ</u> formation of PDC (29, 101), while a more recent report discusses the use of preformed PDC in synthetic applications (33). An advantage in the use of PDC is that it is neither markedly basic or acidic, and in this respect resembles Collins' reagent (31), but is unlike PCC. Due to its ease of preparation and handling, PDC is thus the reagent of choice for oxidations of substrates which contain acid labile substituents.

Because of the generally mild behavior and enhanced selectivity of the organo chlorochromates and dichromates, the ease of preparation, handling, and storing of these reagents, and the ease of isolation of the desired organic product in oxidations where CH_2Cl_2 is used as the solvent, the preparation of new complexes containing the chlorochromate and dichromate anions was undertaken; the preparation of these new complexes is described in chapter IV. The new complexes naphthyridinium chlorochromate (NapCC), pyrazinium chlorochromate (PzCC), pyrazinium-N-oxide chlorochromate (PzOCC), tripyridinium chlorochromate (TPCC), naphthyridinium dichromate (NapDC), and pyrazinium trichromate (PzTC) were reacted with primary, secondary, allylic, and benzylic alcohols, as well as with alkenes to determine the oxidizing ability of each. All of the chromate complexes and the reduced chromium products were insoluble in CH_2Cl_2; thus the desired organic carbonyl compounds could be conveniently isolated by either fractional or vacuum distillation. The results were compared to those obtained using PCC and BPCC.

Experimental

The usual reaction conditions were such that an approximately 4:1 stoichiometric ratio of the Cr(Vl) complex to alcohol was used; the exact mmol quantities are shown in Table XXV.

TABLE XXV

RATIO OF Cr(VI) COMPLEX TO ALCOHOL

	MENTHOL		CYCLOHEXANOL		BENZYL ALCOHOL	
	mmol complex	mmol alcohol	mmol complex	mmol alcohol	mmol complex	mmol alcohol
NapCC	0.26	0.0704	0.165	0.041	0.186	0.041
PzCC	0.163	0.04	0.163	0.041	0.163	0.041
PzOCC	0.22	0.063	0.22	0.054	0.22	0.054
PCC	0.23	0.06	0.23	0.06	0.23	0.06
BPCC	0.17	0.04	0.17	0.042	0.17	0.043
NapDC	0.10	0.02	0.12	0.03	0.12	0.03

	N-PROPANOL		ALLYL ALCOHOL		N-HEPTANOL	
	mmol complex	mmol alcohol	mmol complex	mmol alcohol	mmol complex	mmol alcohol
NapCC	0.183	0.041	0.162	0.041		
PzCC	0.160	0.041	0.156	0.041		
PCC	0.23	0.06	0.23	0.06		
BPCC					0.17	0.04
PzOCC					0.22	0.06
NapDC					0.106	0.019

In a typical reaction the alcohol was weighed on an analytical balance (in the case of menthol) or added via a 10ul syringe to 1.5-2 ml CH_2Cl_2 in a 25 ml round bottom flask equipped with a Teflon coated magnetic stir bar. A gas chromatographic spectrum was recorded of each solution prior to the addition of the Cr(Vl) complex to determine the purity of the sample; all percent conversion calculations were based on these "standard" solutions. Approximately 50 mg of the Cr(Vl) complex was then added to the solution, the round bottom flask was stoppered with a ground glass stopper, and the reaction was shielded from the light. All the reactions were stirred continuously at room temperature using a magnetic stirrer. The starting time of each reaction corresponded to the time at which the Cr(Vl) reagent was added, and the time of each sampling was recorded. All products were identified by the retention times of each product peak compared to known standards run on the same gas chromatographic equipment.

On a larger scale reaction 1 mmol of the alcohol was added as above and 4 mmol of the Cr(Vl) complex was added. After a predetermined period of time the desired organic product was obtained by washing the solution with four 5 ml (193 mmol) volumes of diethyl ether; the decanted ether fractions were filtered, yielding a pale yellow solution. The yellow diethyl ether solution was extracted twice with 5 ml (556 mmol) volumes of H_2O to remove the soluble chromium species. Finally the desired carbonyl compound was obtained by vacuum distillation.

DISCUSSION

The results of the oxidation reactions, given as percent conversion versus time, are shown in Tables XXVI-XXXI; graphical representations of the data are shown in Figures 37-42 at the end of this chapter. An analysis of the data affords some important conclusions regarding the strength of the oxidizing agents--expressed as the rate conversion of the alcohol to its respective carbonyl compound, the change in activity of the oxidizing agent during the reaction time period, and most importantly, the degree of selectivity of the oxidizing agent.

In all cases, the oxidizing strength of the chromates in decreasing order is given by PCC, PzOCC > BPCC > PzCC > NapCC > NapDC > TPCC, PzTC. It is worthy to note that the new chlorochromate PzOCC is an equally strong oxidizing agent as PCC, and that these two species are significantly stronger than all of the other chromate species studied. These observations are likely attributable to the small size of the pyridinium and pyrazinium-N-oxide cations which don't cause considerable shielding of either the metal d orbitals or the oxygens bonded to chromium, and thus don't appreciably restrict the formation of a chromate ester.

The fact that the PzCC is a significantly weaker

TABLE XXVI

OXIDATION OF MENTHOL TO MENTHONE BY Cr(VI) COMPLEXES

NapCC	
% Conv.	Time
6.5	0.45 hr.
16.9	1.32
24.5	1.90
35.8	3.02
38.7	3.68
50.0[a]	4.63
52.1	4.93
67.0	7.27
91.7	19.07

PzCC	
% Conv.	Time
22.1	0.75 hr.
35.7	1.38
43.4	2.50
50.0[a]	2.80
51.8	3.17
63.8	4.34
81.5	6.77

PzOCC	
% Conv.	Time
19.2	0.08 hr.
50.0[a]	0.10
97.4	0.48

PCC	
% Conv.	Time
46.5	0.08 hr.
50.0[a]	0.10
89.9	0.48

BPCC	
% Conv.	Time
29.7	0.25 hr.
44.2	0.50
49.7	0.66
50.0[a]	0.55
64.8	0.92
72.9	1.25
81.6	1.63
93.7	2.66

NapDC	
% Conv.	Time
4.8	0.42 hr.
4.9	1.10
9.0	2.50
14.3	4.70
17.4	5.40
50.0[a]	17.7
65.7	26.5
73.0	73.0
78.0	78.0

TPCC	
% Conv.	Time
0.0	27.0 hr.

[a] These values were determined from the graph of % conversion vs. time.

TABLE XXVII

OXIDATION OF CYCLOHEXANOL TO CYCLOHEXALONE
BY Cr(VI) COMPLEXES

NapCC

% Conv.	Time
13.5	0.17 hr.
22.5	2.08
27.7	3.37
35.3	5.00
37.7	6.00
50.0[a]	9.70

PzCC

% Conv.	Time
19.3	0.72 hr.
31.6	1.55
42.9	2.72
50.0[a]	2.95
69.2	5.50
96.6	7.60

PzOCC

% Conv.	Time
29.0	0.15 hr.
50.0[a]	0.22
100	0.62

PCC

% Conv.	Time
50.0[a]	0.22 hr.
97.0	0.67

BPCC

% Conv.	Time
27.8	0.02 hr.
43.3	0.22
50.0[a]	0.30
59.1	0.45
66.9	1.66

NapDC

% Conv.	Time
1.3	0.1 hr.
3.6	0.6
10.7	2.4
12.0	2.9
16.0	3.6
18.1	6.5
50.0[a]	NA

TPCC

% Conv.	Time
0.0	22.0 hr.

[a] These values were determined from the graph of % conversion vs. time.

NA 50% conversion was not achieved in the time frame of the experiment (see Figure 38)

TABLE XXVIII

OXIDATION OF BENZYL ALCOHOL TO BENZALDEHYDE BY Cr(VI) COMPLEXES

NapCC

% Conv.	Time
46.5	1.58 hr.
50.0[a]	1.76
60.5	2.50
80.6	4.28
86.4	5.35

PzCC

% Conv.	Time
42.4	0.82 hr.
50.0[a]	1.00
61.0	1.78
91.5	2.80

PzOCC

% Conv.	Time
13.5	0.03 hr.
33.0	0.20
50.0[a]	0.10
50.9	0.37
71.0	0.53
89.0	0.70
99.0	0.87

PCC

% Conv.	Time
50.0[a]	0.10 hr.
100.0	0.17

BPCC

% Conv.	Time
19.3	0.02 hr.
42.5	0.22
50.0[a]	0.22
60.5	0.45
73.3	0.53

NapDC

% Conv.	Time
26.1	0.73 hr.
33.6	1.75
42.1	2.50
50.0[a]	3.15
55.6	3.10
54.5	3.60
51.0	4.30
60.0	5.00
60.4	7.10

TPCC

% Conv.	Time
0.0	22.0 hr.

[a] These values were determined from the graph of % conversion vs. time.

TABLE XXIX

OXIDATION OF ALLYL ALCOHOL TO PROPENAL BY Cr(VI) COMPLEXES

NapCC		PzCC		PCC	
% Conv.	Time	% Conv.	Time	% Conv.	Time
23.4	1.00 hr.	11.9	0.42 hr.	50.0[a]	0.05 hr.
37.3	1.83	20.9	1.00	86.0	0.08
44.2	2.67	35.7	2.30		
50.0[a]	2.75	50.0[a]	2.10		
52.2	3.00	81.3	4.40		
70.9	4.67	96.7	5.60		

[a] These values were determined from the graph of % conversion vs. time.

TABLE XXX

OXIDATION OF N-PROPANOL TO PROPANAL BY Cr(VI) COMPLEXES

NapCC		PzCC		PCC	
% Conv.	Time	% Conv.	Time	% Conv.	Time
29.8	1.68 hr.	27.6	0.50 hr.	50.0[a]	0.05 hr.
40.0	3.57	35.8	1.30	86.0	<0.08
47.9	5.33	50.0[a]	1.95		
50.0[a]	6.65	56.7	2.50		
84.0	23.5				
97.8	29.4				

[a] These values were determined from the graph of % conversion vs. time.

TABLE XXXI

OXIDATION OF N-HEPTANOL TO HEPTANAL BY Cr(VI) COMPLEXES

PzOCC		NapDC		BPCC	
% Conv.	Time	% Conv.	Time	% Conv.	Time
49.3	0.15 hr.	11.9	3.50 hr.	25.7	0.70 hr.
50.0[a]	0.15	38.2	22.0	46.7	0.30
92.9	0.55	50.0[a]	NA	50.0[a]	0.30
				57.6	0.47
				66.6	0.63
				73.6	0.82

[a] These values were determined from the graph of % conversion vs. time.

NA 50% conversion was not achieved in the time frame of the experiment (see Figure 42).

oxidizer than PCC or PzOCC seems anomalous based on simple steric considerations. This is perhaps due to the low pKa of pyrazine (pKa = 0.95) causing the proton to spend a significant amount of time on the chromate oxygens, thus decreasing the nucleophillic character of these oxygens (i.e. ester formation or hydrogen ion transfer will be inhibited).

The results also quite clearly show the correlation between the steric demands of the cation and the oxidizing ability of the Cr(VI) for the complexes PCC, BPCC, and TPCC; for all alcohols studied, PCC was a stronger oxidizer than BPCC, which was infinitely stronger than TPCC where the limit of steric demands is achieved or perhaps even exceeded (TPCC failed to oxidize any of the alcohols studied).

NapCC proved to be the weakest of the chlorochromates studied (with the exception of TPCC); this can be attributed to the combined steric bulk of the naphthyridinium cation and its structure. That is, due to the aromatic character of the fused ring system, the naphthyridine is locked into a rigid conformation and may not allow a high degree of exposure of either the metal d orbitals or the chromate oxygens to the alcohol substrate.

The dichromate complex NapDC proved to be a weaker oxidizing agent than all of the chlorochromates except TPCC. This is in good agreement with earlier reports that pyridinium dichromate behaves as a weaker oxidant than PCC (33).

The trichromate complex PzTC proved to be an even weaker oxidant; PzTC failed to oxidize any alcohols in preliminary tests.

Finally, none of the chromate complexes caused further oxidation of aldehydes or ketones to carboxylic acids.

The graphs shown in figures 37-42 indicate that the new chromate complexes PzCC, NapCC, and NapDC show a significant loss in activity with time for the oxidation of 1° and 2° alcohols. This loss in activity increases in the order NapDC > NapCC > PCC for all the alcohols studied. This loss in activity, inversely proportional to time, is what one would expect for a heterogeneous reaction as the reactive sites on the solid surface become depleted. However, PzOCC, like PCC and BPCC shows very little loss in activity with time. This can be attributed to differences in crystal size and thus the total number of active surface sites initially available.

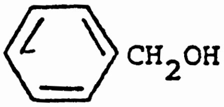
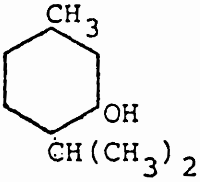
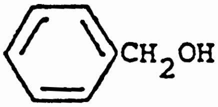
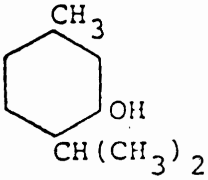
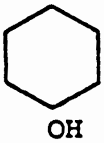
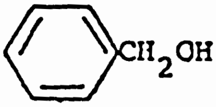
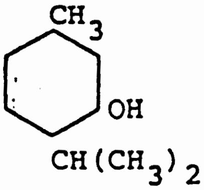
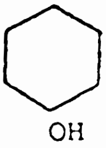
Although this is a perfectly reasonable explanation, it doesn't account for the fact that allyl alcohol and benzyl alcohol are oxidized with much less loss in activity than that observed for the oxidation of other 1° and 2° alcohols by PzCC, NapCC, and NapDC. A plausable reason for this observation may involve the stability of the Cr(V) or Cr(IV) intermediates. That is, the pentavalent or tetravalent states may be stabilized towards further reduction to the trivalent state by interaction with the ligand, thus causing a loss in oxidative activity. Probably, however, both the decay of reactive surface sites and stability of intermediates contribute, but not equally, to the decrease in reactivity with time of the chromate complexes.

Although the strength of an oxidizing agent and its ability to convert alcohols to carbonyl compounds in a reasonable period of time are important characteristics of an oxidizing agent, any deficiencies in these two areas can be overcome simply by using a greater stoichiometric quantity of the oxidant, or even more simply by using a different oxidizing agent altogether. The uniqueness of an oxidizing agent lies not so much in its strength or activity, but in its ability to be stereoselective and to discriminate between two or more similar functions in a multifunctional substrate. The results obtained for the new chromate complexes PzOCC, NapCC, PzCC, and NapDC, compared to those for PCC and BPCC are presented in Table XXXII.

The results show that in all cases, with the exception of PCC, benzyl alcohol is the most easily oxidized alcohol, and that while the equally good oxidizers PCC and PzOCC show slight differences in selectivity, these differences are not significant for synthetic purposes due to the facile oxidation of all alcohols studied by these two reagents. Future applications may show some unique behavior for PzOCC, but our results on the simple alcohols studied don't show any such characteristics.

TABLE XXXII

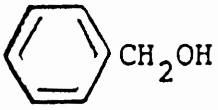
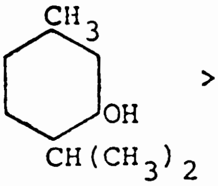
RESULTS FOR FIFTY PERCENT CONVERSION TIMES FOR VARIOUS ALCOHOLS BY PARTICULAR CHROMATE COMPLEXES[a]

Complex	Alcohols				
N-apCC	 (1.76)	> CH$_2$:CHCH$_2$OH > (2.75)	 (4.63)	> CH$_3$CH$_2$CHOH > (6.65)	 (9.70)
PzCC	 (1.00)	> CH$_3$CH$_2$CH$_2$OH > (1.95)	CH$_2$:CHCH$_2$OH > (2.10)	 (2.80) >	 (2.95)
PzOCC	 (0.10)	 (0.10)	> CH$_3$(CH$_2$)$_5$CH$_2$OH > (0.15)	 (0.22)	

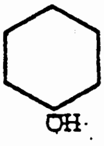
a. The numbers in parentheses correspond to the hours required to accomplish 50% conversion of the alcohol to the respective aldehyde or ketone.

TABLE XXXII (CONT.)

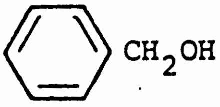
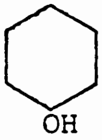
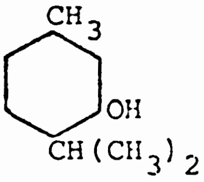
COMPLEX | ALCOHOL

PCC $CH_2{:}CHCH_2OH$, $CH_3CH_2CH_2OH$ >  ,  >

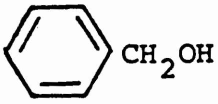
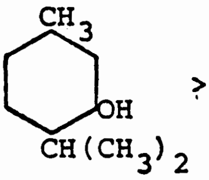
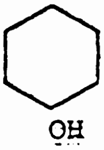
(0.05) (0.05) (0.10) (0.10)



(0.22)

BPCC  > $CH_3(CH_2)_5CH_2OH$,  > 

(0.22) (0.30) (0.30) (0.55)

NapDC  >>  > $CH_3(CH_2)_5CH_2OH$, 

(3.15) (17.7) (NA) (NA)

The times for 50% conversion of alcohols to carbonyl compounds by PzCC show that while it is a much milder oxidizing agent than PzOCC, PCC, or BPCC, it shows only a slight degree of selectivity; PzCC for example converts 50% of the initial benzyl alcohol to benzaldehyde while converting only 26% of the initial methanol and 22% of the initial cyclohexanol to the respective ketones in one hour. Thus the slight preference by PzCC to oxidize benzylic alcohols over 2° alcohols is probably insignificant for synthetic applications.

NapCC is a milder oxidizing agent even then PzCC and shows a greater degree of selectivity. For example, NapCC converts 50% of the initial benzyl alcohol to benzaldehyde during the same time in which it oxidizes only 10% of cyclohexanal to cyclohexanone. In fact, during the time in which 80% of the benzyl alcohol is oxidized, only 17% of the cyclohexanol is oxidized, and this is a significant difference. Thus, there may be some useful synthetic applications for NapCC. This same degree of selectivity isn't however, found for the other 1° and 2° alcohols studied.

The mildest of all the oxidizing agents studied is NapDC, and it also shows the greatest degree of selectivity. The oxidation of benzyl alcohol by NapDC is far more facile than that of 2° alcohols, the next most easily oxidized 2° alcohols showing only 17% conversion of menthol to menthone, and 18% conversion of cyclohexanol to cyclohexanone during the time in which 60% of the initial benzyl alcohol is oxidized to benzaldehyde. Only 38% of the initial 1° alcohol heptanol is oxidized after 22 hr, and only 12% oxidized in the same time in which benzyl alcohol is 53% oxidized. Thus, while NapCC and NapDC both show a similarly strong preference for the oxidation of benzyl alcohol, NapCC shows this preference only compared to cyclohexanol whereas NapDC shows an exclusive preference for the oxidation of benzyl alcohol compared to all other 1° and 2° alcohols studied.

Clearly, NapDC is worthy of further oxidation studies for a wider variety of alcohols than was attempted in our work, particularly for substrates containing more than one alcohol function. NapDC may in fact prove to be a much more useful reagent for the oxidation of benzylic, and perhaps allylic, alcohols than the commonly used MnO_2 which requires very long reaction times and a large excess of the manganese reagent. In addition, the recently reported 4-(dimethylamino)pyridinium chlorochromate complex, which preferentially oxidizes benzylic and allyic alcohols in good yields, suffers from its mildly acidic nature, whereas NapDC, by analogy to PDC, should be neutral in low dielectric solvents. Thus, NapDC may prove to be superior to the 4-(dimethylamino)pyridinium chlorochromate complex, particularly where the organic substrate contains acid labile substituents.

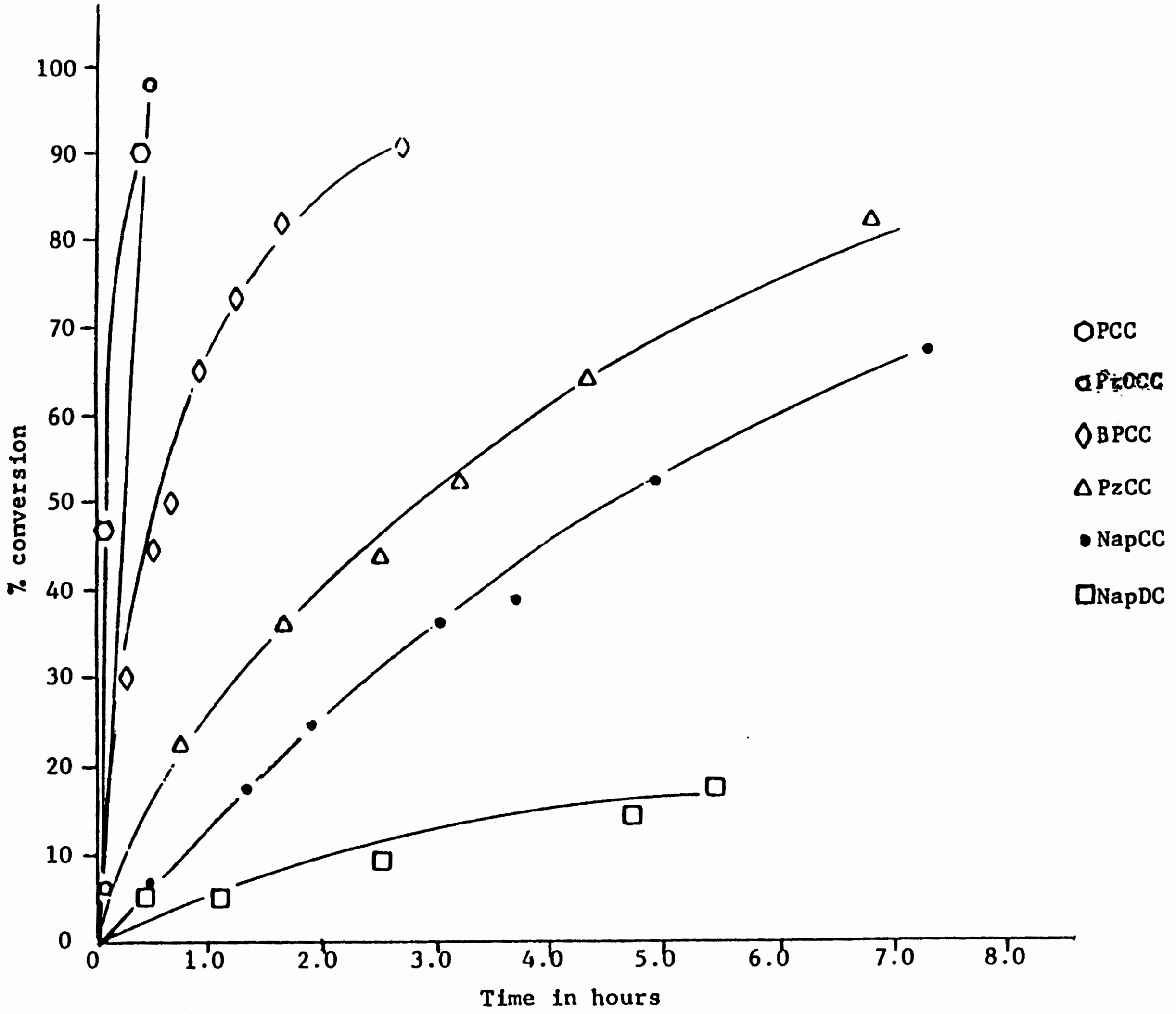


FIGURE 37. Oxidation of menthol by Cr(VI) complexes

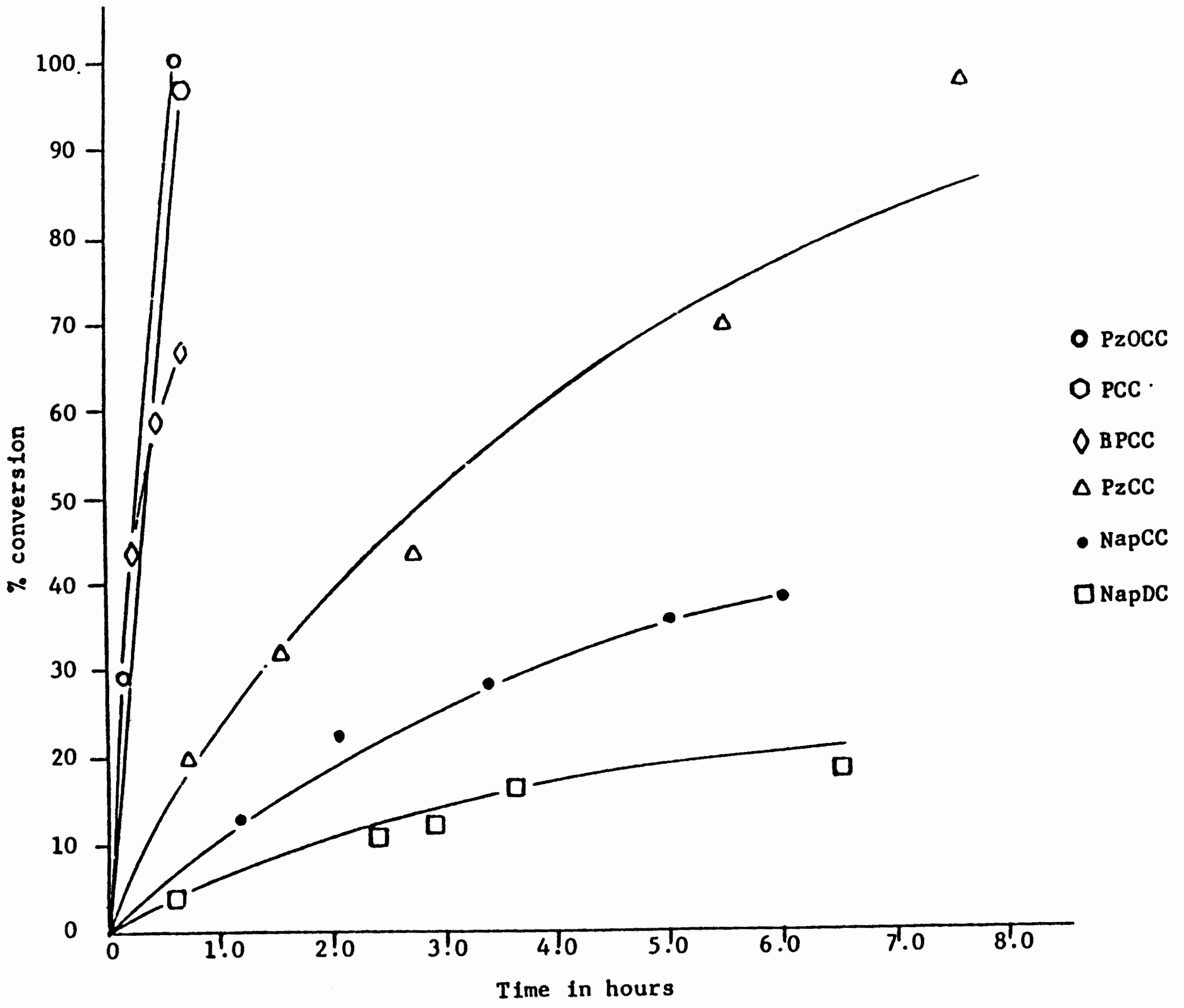


FIGURE 38. Oxidation of cyclohexanol by Cr(VI) complexes

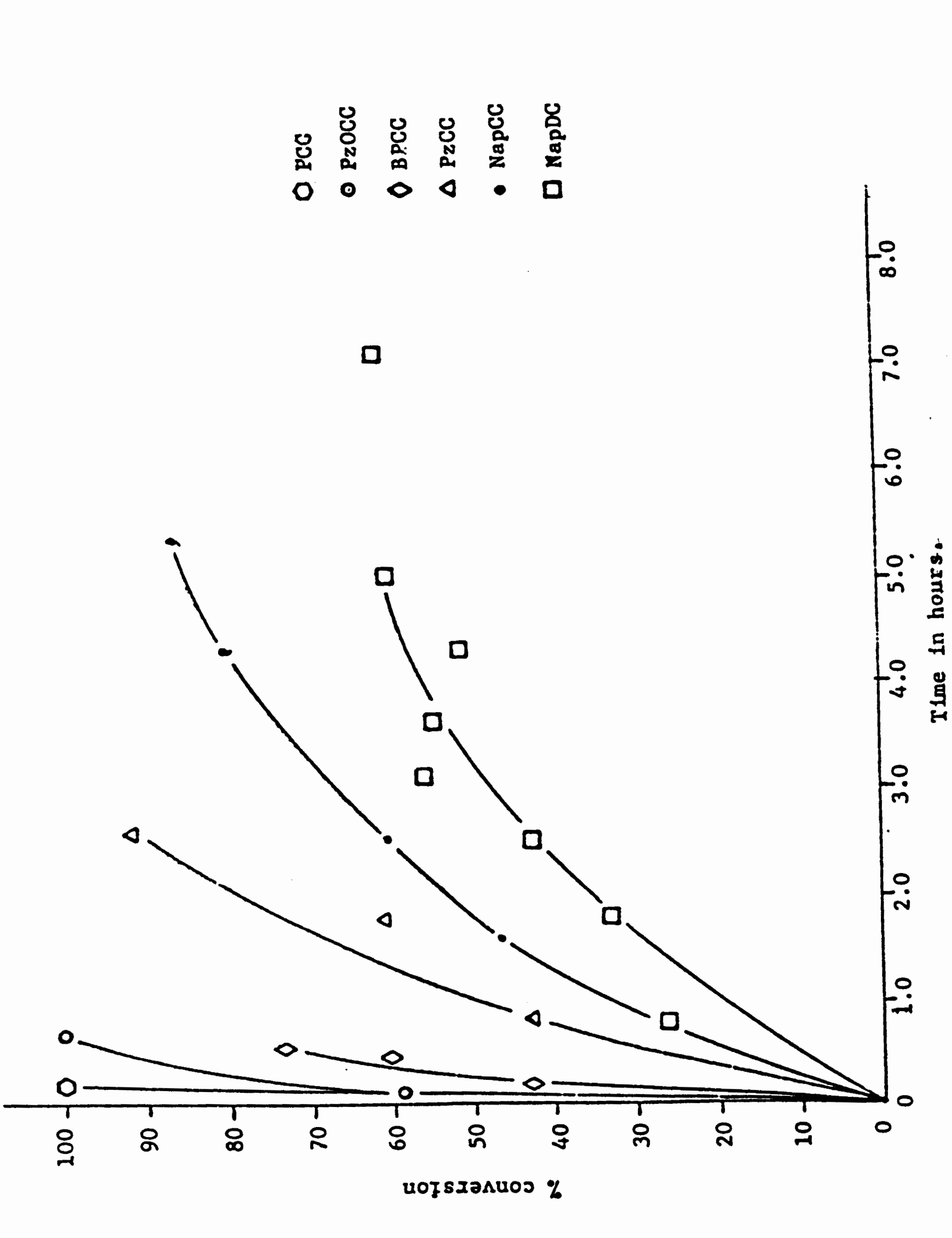


FIGURE 39. Oxidation of benzyl alcohol by Cr(VI) complexes

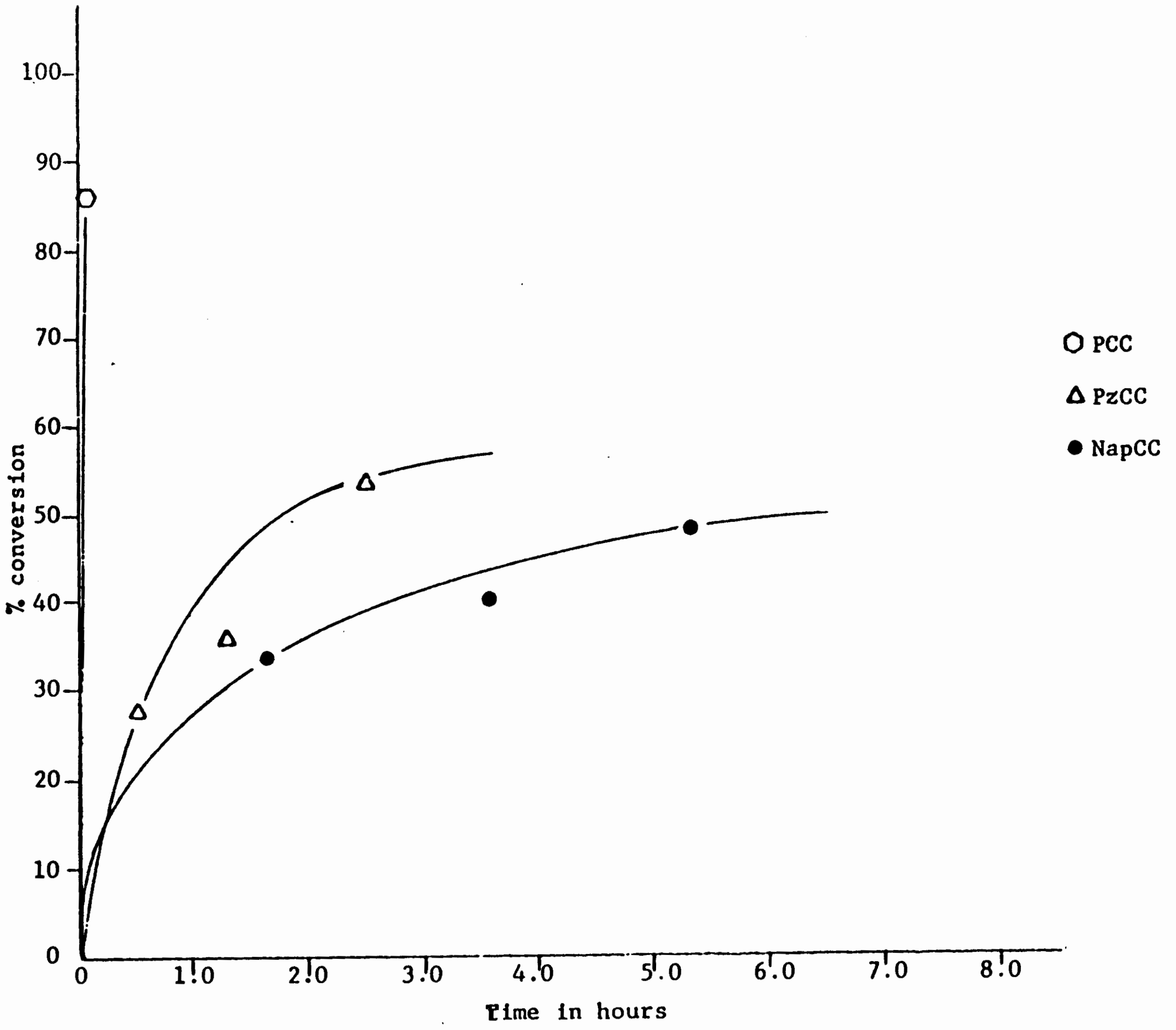


FIGURE 40. Oxidation of n-propanol by Cr(VI) complexes

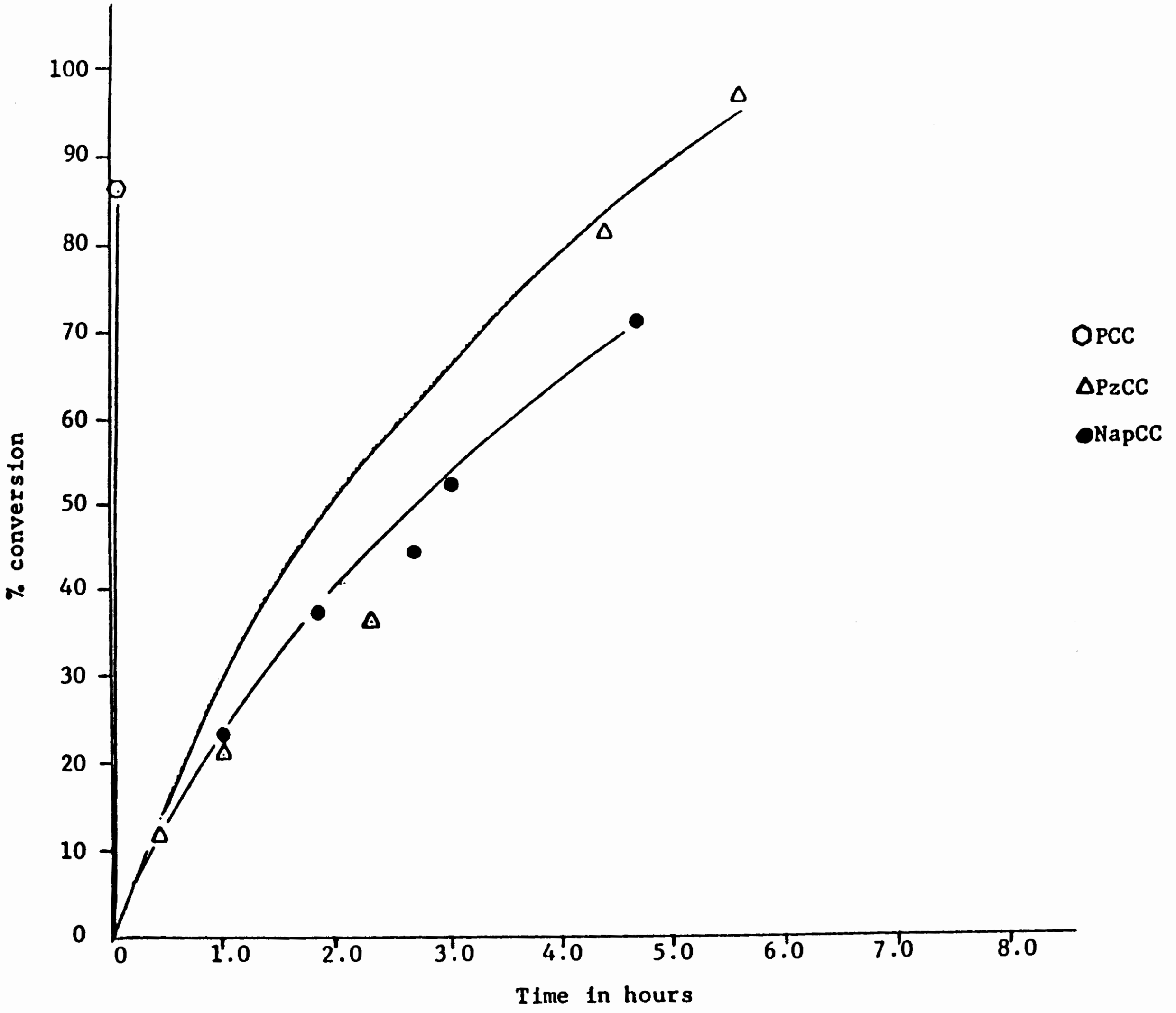


FIGURE 41. Oxidation of allyl alcohol by Cr(VI) complexes

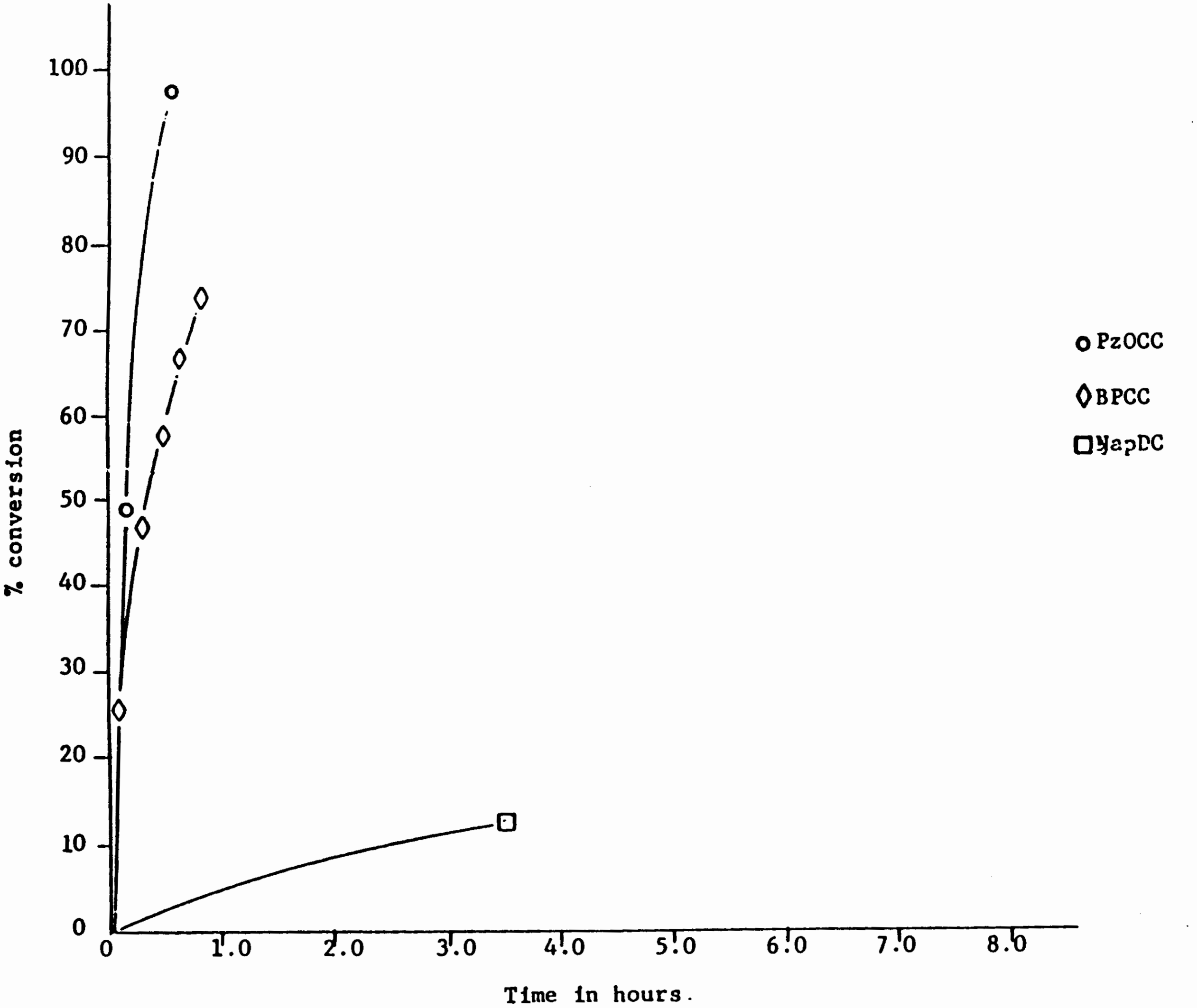


FIGURE 42. Oxidation of n-heptanol by Cr(VI) complexes

REFERENCES CITED

1. Wienland, R. F.; Fiederer, M. Chem. Ber. 1906, 39, 4042.

2. Weinland, R.F.; Fiederer, M. Chem. Ber. 1907, 40, 2090.

3. Ziebarth, O.V.; Selbin, J. J. Inorg. Nucl. Chem. 1970 32, 849.; and references 1-15 therein.

4. Seddon, K. R.; Thomas, V. H. J. Chem. Soc. Dalton Trans. 1977, 2196.; and references 9-12 therein.

5. (a) Sunil, K. K.; Rogers, M. T. Inorg. Chem. 1981, 20, 3283. (b) Sunil, K. K.; Harrison, J. F.; Rogers, M. T. J. Chem. Phys. 1982, 76(6), 3087.

6. Sharpe, A. G.; Woolf, A. A. J. Chem. Soc. 1951, 798. 702.

7. Clark, H. C.; Sadana, Y. N. Can. J. Chem. 1964, 42, 702.

8. Krumpole, M.; DeBoer, B. G.; Rocek, J. J. Am. Chem. Soc. 1978, 100, 145.

9. Willis, C. J. J. Chem. Soc. Chem. Comm. 1972, 944.

10. Mahapatro, S. N.; Krumple, M.; Rocek, J. J. Am. Chem. Soc. 1980, 102-11, 3799.; and references 7 and 13-15 therein.

11. von Wartenberg, H. Z. anorg. allg. Chem. 1941, 247, 135.

12. Slivnik, J.; Zemva, B. Z. anorg. allg. Chem. 1971, 385, 137.

13. (a) Glemser; Roesky; Hellberg; Angew. Chem. 1963; 75, 346. (b) Edwards, A. J. Proc. Chem. Soc. 1963, 205.

14. Edwards, A. J.; Falconer, W. E.; Sunder, W. A. J. Chem Soc. Dalton Trans. 1974, 541.

15. (a) Krauss, H. C.; Munster, G. Z. Naturforsch, 1963, 176, 344. (b) Krauss, H. C.; Leder, M.; Munster, G. Chem. Ber. 1963, 96, 3008.

16. Johannesen, R. B.; Krauss, H. C. Chem. Soc. 1964, 97, 2094.

17. Clark, H. C.; Sadana, Y. N. Can. J. Chem. 1964, 42, 50.

18. Green, P. J.; Johnson, B. M.; Loehr, T. M.; Gard, G. L. Inorg. Chem. 1982, 21, 3562.

19. Johnson, B. M. MS thesis, Portland State University, 1981.

20. Berzelius, J. J. Ann. Phys. Chem. 1824, 1, 34.

21. (a) Etard. Ann. Chim. Phys. 1881, 22, 218. (b) Liebnecht. Chem. Abstracts 1931, 25, 4367.

22. Low; Perkins. J. Chem. Soc. 1907, 91, 191.

23. Sisler, H. H. "Inorganic Synthesis" 1946, 2, 205.

24. San Filipo, J.; Chern, Chuen-Ing. J. Org. Chem. 1977, 42(12), 2182.

25. Rappe, A. K.; Goddard III, W. A. J. Am. Chem. Soc. 1982, 104(2), 448.; and references therein.

26. References 1-6 cited in Edwards, A. J.; Falconer, W. E.; Sunder, W. A. J. Chem Soc. Dalton Trans. 1974, 541.

27. Green, P.J.; Gard, G. L. Inorg. Chem. 1977, 16, 1243.

28. Sisler, H. H.; Buch, J. D.; Accountins, D. E. J. Am. Chem. Soc. 1948, 70, 3827.

29. Poos, G. I.; Arth, G. E.; Beyler, R. E.; Sarrett, L. H. J. Am. Chem. Soc. 1955, 75, 425.

30. Holum, J. R. J. Org. Chem. 1961, 26, 4814.

31. Collins, J. C.; Hess, W. W.; Frank, F. J. Tetrahedron Lett. 1968, 3363.

32. Corey, E. J.; Saggs, J. W. Tetrahedron Lett. 1975, 2647.

33. Corey, E. J.; Schmidt, G. Tetrahedron Lett. 1979, 399.

34. Guziec, F. S.; Luzzio, F. A. Synthesis 1980, 691.

35. Guziec, F. S.; Luzzio, F. A. J. Org. Chem. 1982, 47, 1787.

36. Davis, H. B.; Sheets, R. M.; Brannfors, J. M.; Paudler, W. W.; Gard, G. L. Heterocycles 1983, 20, 2029.

37. Hobbs, W. E. J. Chem. Phys. 1958, 28, 1220.

38. Paudler, W. W.; Kress, T. J. J. Org. Chem. 1967, 32, 832.

39. (a) Petit, G.; Sourlange, C. C. R. Acad. Sci. Ser. C. 1971, 237, 1065. (b) Fiske, T. R.; Baugh, D. W. Dow Chemical Co. U.S. 4, 147, 733, 1979.

40. Rochat, W. V.; Gerlach, J. N.; Gard, G. L. Inorg. Chem. 1970, 9, 998.

41. Engelbrecht, A.; Grosse, A. V. J. Am. Chem. Soc. 1952, 74, 5252.

42. Brown, S. D.; Green, P. J.; Gard, G. L. J. Fluorine Chem. 1975, 5, 203.

43. Green, P. J.; Gard, G. L. Inorg. Nucl. Chem. Lett. 1978, 14, 179.

44. Green, P. J. MSc thesis, Portland State University, 1976.

45. Johnson, B. J. Personal Communication.

46. Atherton, M. J.; Holloway, J. H. J. Chem. Soc. Chem. Comm. 1978, 254.

47. Smith, H. A.; Steinbach, F. C.; Hen, K. E. U.S. Atomic Energy Commission GAT-T-687, 1959.

48. Sicre, J. E.; Schumacher, H. J. Z. anorg. allgm. Chem. 1956, 286, 232.

49. Rakov; Sudarikov; Marinina. Tr. Mosk. Khim. Tekhnol Inst. 1972, 21, 71.

50. Beattie, I. R.; Livingston, A. M. S.; Reynolds, D. J.; Ozin, G. A. J. Chem. Soc. A. 1970, 1210.

51. Blokhim, G. E., Belyaev, J. N.; Opalovskii, A.; Belan, I. Russ. J. Inorg. Chem. (Eng. Transl) 1972, 17, 1113.

52. Brown, S. D.; Gard, G. L.; Loehr, T. M. J. Chem Phys. 1976, 64, 1219.

53. Paine, R. T.; Treuil, K. L.; Stafford, F. E. Spectrochim. Acta. Part A 1973, 29A, 1891.

54. Edwards, A. J.; Taylor, P. Chem. Comm. 1970, 1474.

55. (a) Halloway, J. H.; Schrobilgen, G. J. Inorg. Chem. 1980, 19, 2632. (b) Gillespie, R. J.; Landa, B. Inorg. Chem. 1973, 12, 1383. (c) Gillespie, R. J.; Netzer, A.; Schrobilgen, G. J. Inorg. Chem. 1974, 13, 1455. (d) Gillespie, R. J.; Schrobilgen, G. J. Inorg. Chem. 1974, 13, 2370. (e) Gillespie, R. J.; Schrobilgen, G. J. Inorg. Chem. 1974, 13, 765.

56. Tucker, P. A.; Taylor, P. A.; Holloway, J. H.; Russell, D. R. Acta. Cryst. 1975, B31, 906.

57. Holloway, J. H.; Schrobilgen, G. J.; Taylor, P. J. Chem. Soc. Chem. Comm. 1975, 40.

58. McRae, V. M.; Peacock, R. D.; Russell, D. R. J. Chem. Soc. Chem. Comm. 1962, 62.

59. Howell, J. A. S.; Moss, K. C. J. Chem Soc. A. 1971, 270.

60. Garner, C. D.; Kendrick, J.; Lambert, P.; Mabbs, F. E.; Hillier, I. H. Inorg. Chem. 1976, 15, 1287.

61. Bartlett, N.; Jha, N. K. J. Chem. Soc. A. 1968, 536.; and references therein.

62. Corey, E. J.; Boger, Dale L. Tetrahedran Lett., 1978, 2461.

63. (a) Dauben, W. G. J. Org. Chem. 1977, 42, 652. (b) Plancatelli, G.; Scettri, A.; Auria, M. D. Tetrahedran Lett. 1977, 2129.

64. Epstein, J. M.; Dewan, J. C.; Kepert, D. L.; White, A. H. J. Chem. Soc. Dalton Trans. 1974, 18, 1949.

65. (a) Carmichael, W. M.; Edwards, D. A. J. Inorg. Nucl. Chem. 1970, 32, 1199. (b) Belford, R. C. E.; Fenton, D. E.; Truter, M. R. J. Chem Soc. Dalton Trans. 1974, 17 (c) Lever, A. B. P.; Lewis, J.; Nyholm, R. S. J. Inorg. Nucl. Chem. 1961, 18, 238.

66. Specca, A. N.; Pytlewski, L. L.; Karayannis, N. M. J. Inorg. Nucl. Chem. 1973, 35, 4029.

67. Dvoryantseva, G. G.; Kaganskii, M. M.; Musatova, L. S.; Elina, A. S. Khim. Geterofsikl. Soedin. 1974, 11, 1554.

68. Ul'yanova, T. N.; Dvoryantseva, G. G.; Alekseeva, L. M.; Sheinker, Yu. N.; Elima, A. S. Khim. Geterotikl. Soedin. 1971, 7(6), 846.

69. Kaganskii, M. M.; Dvoryantseva, G. G.; Elima, A. S. Akad. Naak. SSSR. 1971, 197(4), 832.

70. Cotton, F. Albert, and Wilkinson, Geoffrey. "Advanced Inorganic Chemistry," 4th ed., John Wiley & Sons, 1980.

71. Pearson, R. G. J. Am. Chem. Soc. 1963, 85, 3533.

72. Huheey, James E., "Inorganic Chemistry: Principles of Structure and Reactivity," 2nd ed., Harper & Row, 1972.

73. Armarego, W. L. F.; Barlin, G. B.; Spinner, E. Spectrochim. Acta. 1966, 22, 117.

74. Califano, S.; Adembri, G.; Sbrana, G. Spectrochim. Acta 1964, 20, 385.

75. Lord, R. C.; Marston, A. L.; Millers, F. A. Spectrochim. Acta 1957, 9, 113.

76. This reaction was carried out by Roger M. Sheets.

77. Helmholtz, L.; Foster, W. B. J. Am. Chem. Soc. 1950, 72, 4971.

78. Stammreich, H.; Sala, O.; Kawak, K. Spectrochim. Acta 1961, 17, 226.

79. McCaln, D. C. J. Phys. Chem. 1975, 79(11), 1102.

80. Herlocker, D. W.; Drago, R. S.; Imhof-Meek, V. Inorg. Chem. 1968, 5, 2009.

81. (a) Dvoryantseva, G. G.; Kaganskii, M. M.; Musatova, L. S.; Elima, A. S. Khim. Geterofsikl. Soedin. 1974, 11, 1554. (b) Ul'yanova, T. N.; Dvoryantseva, G. G.; Alekseeva, L. M.; Sheinkar, Yu. N.; Elima, A. S. Khim. Geterofsikl. Soedin. 1971, 7(6), 846.

82. Semmer, R.; Mitzner, R. Z. Chem. 1978, 18, 192.

83. Colthrup, N. B.; Daly, L. H.; Wiberly, S. E. "Introduction to Infrared and Raman Spectroscopy." Academic Press, New York, 1964.

84. Stammreich, H.; Bassi, D.; Sala, O.; Siebert, H. Spectrochim. Acta 1958, 13, 192.

85. Radhakrishna, S.; Sharma, B. D. Chem. Phys. Lett. 1972, 17(4), 578.

86. Mattes, R. Z. anorg. allg. Chem. 1971, 382, 163.

87. Lofgren, P. Chemica Scripta. 1974, 5, 91.

88. Goldstein, M.; Unsworth, W. D. Spectrochim. Acta 1971, 27A, 1055.

89. Makhija, R. C.; Stairs, R. A. Can. J. Chem. 1968, 46, 1255.

90. Vranka, R. G.; Amma, E. L. Inorg. Chem. 1966, 5, 1020.

91. Trust, B.; Lautens, M. Ind. Chem. News 1983, 4(6), 1.

92. (a) Willis, J. P.; Gogins, K. A. Z.; Miller L. L. J. Org. Chem. 1981, 46, 3215. (b) Herscovic, J.; Antonaris, K. J. Chem. Soc. Chem. Comm. 1980, 561. (c) Frechet, J. M. J.; Darling, P.; Farrall, M. J. J. Org. Chem. 1981, 46, 1728. (d) Frechet, J. M. J.; Warnock, J.; Farrall, M. J. J. Org. Chem. 1979, 43, 2619. (e) Corey, E. J.; Boger, D. L. Tetrahedron Lett. 1978, 28, 2461.

93. Dauben, W. G.; Lorber, M.; Fullerton, D. S. J. Org. Chem. 1969, 34(11), 3587.

94. (a) Baker, L. M.; Carrick, W. L. J. Org. Chem. 1968, 33(2), 616. (b) Baker, L. M.; Carrick, W. L. J. Org. Chem. 1970, 35(3), 774.

95. (a) Cohen, M.; Westheimer, F. H., J. Am. Chem. Soc. 1952, 74, 4387. (b) Holloway, F.; Cohen, M.; Westheimer, F. H. J. Am. Chem. Soc. 1951, 73, 65. (c) Westheimer, F. H. Chem. Rev. 1949, 45, 419.

96. (a) Srinivasen, V.; Rocek, J. J. Am. Chem. Soc. 1974, 96(1), 127. (b) Wiberg, K. B.; Schafer, H. J. Am. Chem. Soc. 1969, 91(4) 933. (c) Rocek, J.; Ip, D. J. Am. Chem. Soc. 1979, 101(21), 6311. (d) Wiberg, K. B. "Oxidations in Organic Chemistry" Academic Press, New York, N.Y. 1965.

97. (a) Bobteisky, M.; Radovensky-Cholatnikow, C. Z anorg. allgm. Chem. 1931, 199, 241. (b) Westheimer, F. H.; Novick, A. J. Chem. Phys. 1943, 11, 506.

98. Lee, D. G.; Stewart, R. J. Am. Chem. Soc. 1964, 86 (15), 3051.

99. Watanabe, W.; Westheimer, F. H. J. Am. Chem. Soc. 1939, 61, 555.

100. Watanabe, W. PhD dissertation, Chicago, 1948.

101. (a) Cornforth, R. H.; Cornforth, J. W.; Popjak, G. Tetrahedron Lett. 1962, 18, 1351. (b) Coates, W. M.; Corrigan, J. R. Chem. and Ind. 1969, 1594.