Journal of Fluorine Chemistry, 5 (1975) 203 – 220

Received: April 18, 1974

THE CHEMISTRY OF CHROMYL FLUORIDE

III. REACTIONS WITH INORGANIC SYSTEMS*

STEVEN D. BROWN**, PATRICK J. GREEN** and G.L. GARD***

Department of Chemistry, Portland State University, Portland, Oregon (U.S.A.)

SUMMARY

Reactions of CrO_2F_2 with MF or MF_2 gave the corresponding $M_2CrO_2F_4$ and $MCrO_2F_4$ fluorochromates. With the Lewis Acids (SO_3, TaF_5, SbF_5) and $(CF_3CO)_2O$ known and new chromyl compounds [$CrO_2(CF_3COO)_2$, $CrO_2(SO_3F)_2$, CrO_2FTaF_6, CrO_2FSbF_6, $CrO_2FSb_2F_{11}$] were produced. Chromyl fluoride and inorganic salts (CF_3COONa and $NaNO_3$) produced the following complexes - $Na_2CrO_2F_2(CF_3COO)_2$ and $Na_2CrO_2F_2(NO_3)_2$. Unusual solid products were obtained with CrO_2F_2 and NO, NO_2, SO_2.

A new method of preparing CrO_2F_2 is also presented.

INTRODUCTION

The literature dealing with chromyl compounds covers essentially chromyl chloride (CrO_2Cl_2) and its reactions. The fluorine analog of

---

* Presented at the 7th International Symposium on Fluorine Chemistry, Santa Cruz, California. Part II: S.D. Brown and G.L. Gard, Inorg. Chem., 12, 483 (1973).

** PRF Undergraduate Scholar.

*** To whom inquiries should be addressed.

CrO_2Cl_2, chromyl fluoride (CrO_2F_2) has received far less attention and it was not until 1952 that its physical properties were accurately determined.[1] Prior to this work the literature concerning CrO_2F_2 was full of conflicting and sketchy information and even today very little information is known about its chemical properties.

Unverdorben [2] found that CrO_2F_2 is reduced by arsenic trioxide, forming arsenic fluorides and chromic oxide. Also, he found that CrO_2F_2 exchanges its fluorines with numerous metal oxides, forming BF_3 from boric oxide and SiF_4 from glass.[3]

CrO_2F_2 is described as a strong fluorinating agent.[4] However, this report as well as earlier reports are likely to be erroneous because CrO_2F_2 was contaminated with fluorine.

Flesch and Svec [5] produced CrO_2ClF from CrO_2F_2 and CrO_2Cl_2. Grosse [1] reported that CrO_2F_2 does not react with KF or NaF at room temperature, but with KHF_2 and $NaHF_2$ produced $CrO_2F_2 \cdot KHF_2$ and $CrO_2F_2 \cdot NaHF_2$ complexes.

These studies encompassed all that was known about CrO_2F_2 prior to our investigations.

RESULTS AND DISCUSSION

For most of our studies the CrO_2F_2 was prepared by essentially the method of Flesch and Svec.[5] However, an equally direct and perhaps more convenient method is the following:

$$CrO_2Cl_2 + 2ClF \overset{-78}{=} CrO_2F_2 + 2Cl_2 \qquad (1)$$

Large quantities of pure CrO_2F_2 have been prepared in this manner.

We have found that under proper conditions CrO_2F_2 will react with Group IA and Group IIA metal fluorides generally producing orange colored solid fluorochromates in essentially 100% yield according to the following equations:

$$2MF + CrO_2F_2 = M_2CrO_2F_4 \tag{2}$$

$M = Na, K, Cs$

$$MF_2 + CrO_2F_2 = MCrO_2F_4 \tag{3}$$

$M = Ca, Mg$

Although these new salts can be prepared directly, the solvent perfluoroheptane (C_7F_{16}) facilitates their formation. In this respect CrO_2F_2 behaves like UF_6 in its reaction with metal fluorides where perfluoroheptane was needed to ensure complete reaction.[6]

These new compounds fume in moist air and hydrolyze in water giving yellow dichromate solutions. Also, they react with organic compounds producing brownish products that were not investigated. LiF did not react under comparable conditions.

In addition to reacting with metal fluorides (Lewis Bases), chromyl fluoride reacts with $(CF_3CO)_2O$ or various Lewis acids according to the equations:

$$CrO_2F_2 + 2(CF_3CO)_2O = CrO_2(CF_3COO)_2 + 2CF_3COF \tag{4}$$

$$CrO_2F_2 + 2SO_3 = CrO_2(SO_3F)_2 \tag{5}$$

$$CrO_2F_2 + TaF_5 = CrO_2F_2 \cdot TaF_5 \tag{6}$$

$$CrO_2F_2 + SbF_5 = CrO_2F_2 \cdot SbF_5 \tag{7}$$

$$CrO_2F_2 + 2SbF_5 = CrO_2F_2 \cdot 2SbF_5 \tag{8}$$

These solid compounds are regarded as chromyl compounds and are quite reactive with water producing yellow dichromate solutions. In the reaction with other weaker Lewis Acids (PF_5, BF_3, AsF_5) no reaction was evident at room temperature.

By analogy to the reaction of CrO_2F_2 with metal fluorides it was found that other salts (CF_3COONa, $NaNO_3$, and NaCl) would react similarly producing new fluorochromates. For CF_3COONa and $NaNO_3$ the following reactions were found:

$$CrO_2F_2 + 2CF_3COONa \xrightarrow{CF_3COOH} Na_2CrO_2F_2(CF_3COO)_2 \quad (9)$$

$$CrO_2F_2 + 2NaNO_3 \xrightarrow{C_7F_{16}} Na_2CrO_2F_2(NO_3)_2 \quad (10)$$

However, with NaCl only CrO_2Cl_2 and $Na_2CrO_2F_4$ were formed at room temperature.

$$2CrO_2F_2 + 2NaCl = CrO_2Cl_2 + Na_2CrO_2F_4 \quad (11)$$

In reference to equation 10, it is interesting that without the solvent C_7F_{16} and with excess CrO_2F_2, $CrO_2(NO_3)_2$ and $Na_2CrO_2F_4$ were formed.[7] Therefore, in addition to producing new fluorochromates there is a possibility of forming chromyl compounds from CrO_2F_2 and inorganic salts.

Chromyl compounds are powerful oxidizing agents and as such react vigorously with NO, NO_2, and SO_2 according to the following equations:

$$NO + CrO_2F_2 = NO\cdot CrO_2F_2 \quad (12)$$

$$2NO_2 + CrO_2F_2 = (NO_2)_2\cdot CrO_2F_2 \quad (13)$$

$$SO_2 + 2CrO_2F_2 = SO_2\cdot 2CrO_2F_2 \quad (14)$$

The products formed in the above reactions are all amorphous solids which when hydrolyzed in water give a yellow-green solution. There are no gaseous by-products formed. The properties of the above products parallel those obtained from the reaction of organic molecules with CrO_2Cl_2 in which the chromium is in an oxidation state of (IV).[8] Magnetic susceptibility measurements for these complexes (see Table I) strongly suggest that the chromium in $(NO_2)_2\cdot CrO_2F_2$ is in an oxidation state of four while for $SO_2\cdot 2CrO_2F_2$ and $NO\cdot CrO_2F_2$ the oxidation state of five. The lower oxidation states account for the yellow-green solution produced upon hydrolysis.

The x-ray powder spectra of the fluorochromates produced in reactions (2) and (3) showed the presence of new compounds and rules out a physical mixture.

The infrared spectra of the fluorochromates (presumably octahedrally coordinated) are tabulated in Table II. Griffith [9] has found that all known octahedral mononuclear transition-metal (d°) dioxo complexes possess

TABLE I

Magnetic Susceptibilities
of Inorganic Chromium Complexes

	Expt'l, eff (B.M.)*
$NO \cdot CrO_2F_2$	1.79 ‡
$(NO_2)_2 \cdot CrO_2F_2$	3.12
$SO_2 \cdot 2CrO_2F_2$	2.73

The theoretical μeff for Cr^{+4} is 2.83 B.M.

‡ Heating $NO \cdot CrO_2F_2$ for 16 hrs. at 65° increased the μeff to 2.91 B.M. Evidently the $NOCrO_2F_2$ is slowly converted in part to NO_2CrOF_2.

the cis- and the d^2 transition-metal dioxo complexes the trans dioxo structure. For the octahedral cis-dioxo compounds (symmetry C_{2v}) the $\nu_s(MO_2)$ and $\delta(MO_2)$ are A_1 modes and $\nu_{as}(MO_2)$ is B_1; all three are active in the i.r. For the compounds $Na_2WO_2F_4$ and $Na_2MoO_2F_4$, $\nu_s(MO_2)$ and $\nu_{as}(MO_2)$ were found at 951 and 958 cm^{-1} and 904 and 920 cm^{-1} respectively.[9] Assuming the fluorochromates (Cr VI, d°) possess the cis-dioxo structure the correspondong sym. and asym., MO_2 stretching vibrations should be infrared active and have similar frequencies and intensities. For the alkali metal fluorochromates (see Table II) MO_2 vibrations and intensities (ν_s 935-955 cm^{-1}; ν_{as} 910-915 cm^{-1}) similar to $Na_2WO_2F_4$ and $Na_2Mo_2F_4$ are found. This result strongly supports a cis-dioxo structure for these salts. There are additional bands similar to the O=Cr=O vibrations particularly for $Na_2CrO_2F_4$, $K_2CrO_2F_4$ and $CaCrO_2F_4$. These may be due to interaction between Cr=O groups in neighboring molecules. Makhija and Stairs came to a similar conclusion for their reported chromyl chloride triphenylphosphine and triphenylarsine complexes.[10] The $\delta(MO_2)$ deformation bands for the

TABLE II

Infrared Spectra of CrO_2F_2 and Lewis Base Products (cm^{-1})

$Na_2CrO_2F_4$	$K_2CrO_2F_4$	$Cs_2CrO_2F_4$
1200 (m)	1034 (m)	946 (s) with sh. 1000 cm^{-1}
955 (s)	955 (s)	910 (m)
935 (m)	915 (m)	631 (s,b)
910 (m)	635 (s,b)	500 (m,b)
720 (w)	315 (w,b)	330 (w)
580 (s,b)		
467 (w)		
380 (w,b)		

$MgCrO_2F_2$	$CaCrO_2F_4$	$Na_2CrO_2(CF_3COO)_2F_2$
948 (s)	1230 (w)	1620 (m)
899 (w)	976 (s) with sh at 990	1429 (w)
825 (w)	968 (s) with sh. at 940	1350 (w)
740 (m,b)	890 (w-m)	1160 (s)
450 (s,b)	825 (m,b)	935 (m)
400 (s)	470-300 (s,b)	844 (w)
		807 (w)
		704 (w,b)

$Na_2CrO_2(NO_3)_2F_2$ ‡
1630 (w)
1350 (s)
963 (m,b)
899 (w)
875 (w)
833 (m)

‡ See ref. 7 for preparation of this compound.

alkali metal fluorochromates are found in the 315-380 cm^{-1} region. For $Na_2WO_2F_4$ and $Na_2MoO_2F_4$, the $\delta(MO_2)$ deformation bands are found at 378 cm^{-1} and 385 cm^{-1}, respectively.[9]

The infrared spectra of the new chromyl compounds produced in reactions (6), (7) and (8) are given in Table III. The spectra of $CrO_2(SO_3F)_2$ and $CrO_2(CF_3COO)_2$ agreed with previously reported values.[11,12] For $CrO_2F_2 \cdot SbF_5$ and $CrO_2F_2 \cdot 2SbF_5$ the sym. [$v_s(MO_2)$] metal-oxygen vibrations are located at 950 and 940 cm^{-1}. The asym. [$\nu_{as}(MO_2)$] metal-oxygen vibrations are found at 970 and 955 cm^{-1}. By comparison, CrO_2F_2 sym. and asym. metal-oxygen vibrations are at 1006 and 1017 cm^{-1}, [13] while in $KCrO_3F$ they are found at 912 and 952 cm^{-1}.[14]

The Raman spectra for $CrO_2F_2 \cdot SbF_5$ and $CrO_2F_2 \cdot 2SbF_5$ were obtained under instrumental conditions of low sensitivity over a range of 300-1200 cm^{-1}. The observed frequencies (cm^{-1}) and relative intensities for $CrO_2F_2 \cdot SbF_5$ are located at 663 (s), 940 (m), 960 (s) and for $CrO_2F_2 \cdot 2SbF_5$ are at 660 (s), 697 (m-s) and 945 (s). For the $CrO_2F_2 \cdot SbF_5$ complex the Raman line at 663 cm^{-1} is characteristic for the SbF_6^- ion. In $KSbF_6$ [15] and O_2SbF_6 [16] the Raman lines are located at 661 cm^{-1} and 656 cm^{-1}, respectively. The 940 cm^{-1} and 960 cm^{-1} lines are due to Cr-O stretching frequencies.

For the $CrO_2F_2 \cdot 2SbF_5$ complex the Raman lines at 660 cm^{-1} and 697 cm^{-1} are characteristic of the $Sb_2F_{11}^-$ ion. In $KrFSb_2F_{11}$ [17] these Raman lines are located at 693 cm^{-1} and 679 cm^{-1}, while for $O_2Sb_2F_{11}$ [16] they are found at 688 cm^{-1} and 659 cm^{-1}. The 945 cm^{-1} absorption is attributable to the Cr-O stretching mode.

The Raman results strongly suggest that for the 1:1 and 1:2 complexes, SbF_6^- and $Sb_2F_{11}^-$ anions are present, respectively. The cation characteris-

TABLE III

Lewis Acid Products (cm^{-1}) Infrared Spectra of CrO_2F_2 and

$CrO_2F(SbF_6)$	$CrO_2F(Sb_2F_{11})$	$CrO_2F(TaF_6)$
970 (s)	955 (s)	934 (s)
950 (s)	940 (s)	895 (m)
710 (s,b)	690 (s,b)	573 (s,vb)
620 (s,b)	655 (s,b)	
570 (s)	550 (s,b)	
525 (s,b) with sh. at 505	510 (s,b)	
477 (m)	460 (m)	
375 (w-m)	304 (m)	
304 (m)		

TABLE IV

Infrared Spectra of Inorganic Chromium Complexes (cm^{-1})

$NO\cdot CrO_2F_2$	$(NO_2)_2CrO_2F_2$ ‡	$SO_2\cdot 2CrO_2F_2$
2280 (vw)	2340 (m)	1360 (s)
1600 (w)	1600 (m)	1310 (w)
1475 (s)	1485 (m)	1130 (s)
1280 (s)	1265 (s) with sh.	1050 (s,b)
960 (m,b)	at 1190 (m)	974 (s,b)
860 (w,b)	955 (s)	838 (m)
762 (w,b)	550 (s)	699 (m)
535 (s,b)		

‡ See reference 7 for preparation of this compound.

tic of both solids would be CrO_2F^+. This interpretation would not rule out fluorine bridge bonding between Cr and Sb thereby increasing the coordinumber around Cr to four.

For $CrO_2F_2\cdot TaF_5$ the sym. and asym. metal-oxygen vibrations are at 895 and 934 cm^{-1}, respectively. The strong band centered at 573 cm^{-1} is probably the Ta-F stretching vibration which is located at 582 cm^{-1} in the TaF_6^- ion.[18] This evidence favors the formulation of $CrO_2F_2\cdot TaF_5$ as $CrO_2F^+TaF_6^-$.

The infrared spectrum of $Na_2CrO_2F_2(CF_3COO)_2$ given in Table II shows the COO asymmetric stretch at 1620 cm^{-1} while the COO symmetric stretch is probably at 1350 cm^{-1}. The C-F asymmetric stretch occurs at 1160 cm^{-1} with the CF_3 symmetric stretch at 807 cm^{-1}. The absorption band at 844 cm^{-1} is the C-C stretch and the one at 704 cm^{-1} the CCO_2 in-plane bend. The 935 cm^{-1} band represents the Cr-O stretch. The infrared spectrum and assignments of $Na_2CrO_2F_2(CF_3COO)_2$ are very similar to other oxychromium trifluoroacetate salts [i.e. $K_2CrO_2(CF_3COO)_4$] previously reported.[19]

For $Na_2CrO_2F_2(NO_3)_2$ in Table II, the absorption band at 1350 cm^{-1} is probably the asymmetric N-O stretching vibration and the absorption band at

833 cm^{-1}, the out-of-plane N-O bending vibration.[20] The absorption at 963 cm^{-1} is the Cr-O stretching vibration.

The broad absorption bands for $(NO_2)_2CrO_2F_2$, $NO \cdot CrO_2F_2$, and $SO_2 \cdot 2CrO_2F_2$ at 955 cm^{-1}, 980 cm^{-1}, and 974 cm^{-1} respectively represent the Cr-O stretching vibrations. Although additional tentative assignments can be made for these complexes [e.g. the absorption bands at 2360 cm^{-1} and 550 cm^{-1} in $(NO_2)_2CrO_2F_2$ are attributable to NO_2^+ and the absorption bands at 1485 cm^{-1} and 1265 cm^{-1} are attributable to bridging NO_2 groups; the absorption band for $NO \cdot CrO_2F_2$ at 2280 cm^{-1} is attributable to NO^+; for the $SO_2 \cdot CrO_2F_2$ complex the absorption bands at 1130 cm^{-1} and 1050 cm^{-1} are probably the sym. and asym. S-O vibrations] it is impossible to draw any conclusions regarding the structures of these complexes.

EXPERIMENTAL SECTION

Chemicals and Equipment

The salts NaF, NaCl, CaF_2 and $NaNO_3$ used in this study were obtained from Mallinckrodt and were reagent grade. They were thoroughly dried immediately before use. PF_5, CsF, CF_3COONa, TaF_5, and C_7F_{16} were purchased from Penninsular Chem Research and were of 98% purity; the CsF was dried before use. CrO_2Cl_2, MgF_2, and KF were obtained from Alpha Inorganic Chemicals. The MgF_2 and KF were dried thoroughly before use; the CrO_2Cl_2 was distilled from Hg. SO_3 was obtained from J. Baker Chemicals and was vacuum distilled before use. The BF_3, NO_2, and SO_2 were obtained from Matheson and were used as received. The NO was obtained from Air Products and Chemicals. NO was purified by repeated trap to trap distillation.

The infrared spectra were recorded on a Perkin-Elmer 467 infrared spectrophotometer. Infrared spectra of gaseous samples were obtained with a monel cell (NaCl windows) equipped with a Whitney Brass valve. The path length of the cell was 8.25 cm. The spectra of solid samples were obtained neat between either NaCl, BaF_2 or CsBr windows. The spectra were calibrated with a polystyrene film.

The Raman spectra were measured with a Jarrell Ash 25-300 Raman spectrometer using a Spectra-Physics 250 helium-neon laser for excitation at 6328 Å. The scattered radiation was detected at right angles to the incident beam (transverse viewing, axial excitation) by means of a thermoelectrically cooled S-20 photomultiplier tube and photon counting system. Both $CrO_2F_2 \cdot SbF_5$ and $CrO_2F_2 \cdot 2SbF_5$ were contained as solids in 5-mm o.d. "optically flat" pyrex cells at room temperature. The spectral slit width was 12 cm^{-1}.

The magnetic susceptibility values were obtained by the Gouy method. Measurements were made at a field strength of about 5 KG using an Alpha AL 7500 water-cooled magnet with 4-in. pole faces and a 1.5-in. air gap. The Gouy tube was calibrated at room temperature ($\sim 23°$) and the gram-susceptibility of the calibrant, mercury(II)tetrathiocyanatocobalate(II), was calculated using the data cited by Cotton, et al.[21] Diamagnetic corrections were made using Pascal's constants. The procedure was standardized using $CuSO_4 \cdot 5H_2O$ in which the calculated magnetic susceptibility agreed with the known value.

X-ray powder spectra were obtained using an XRD-5 General Electric camera. Nickel-filtered $CuK\alpha$ radiation was used. The procedure was standardized using known compounds (CrO_3, Cr_2O_3, $CrF_3 \cdot H_2O$) in which the calculated d values agreed with the published ASTM values. Only the very strong (vs), strong (s), and medium (m) intensity lines are reported in this paper.

Chemical Analyses

The chromium content was determined idometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. The acidity was determined by titration with a standard base solution using phenophthalein indicator. Standard analyses were performed by Beller Laboratories, Göttingen, West Germany.

Preparation of CrO_2F_2

To 31.0 mmol of CrO_2Cl_2 in a 30 ml Hoke vessel equipped with an Autoclave spacesaver valve, 64.0 mmol of ClF was added. The reactant materials were kept at -78° for 24 hr. The volatile materials (Cl_2 and ClF were pumped away at -78°. The CrO_2F_2 (30.6 mmol) was formed in essentially 100% yield.

The infrared spectrum agreed with the literature.[13]

Anal. Calcd for CrO_2F_2: Cr, 42.6. Found: Cr, 42.7 via iodometry, 42.3 via acidity.

Preparation of $K_2CrO_2F_4$*

To 13.9 mmol of dried KF in a ~125 ml polyethylene vessel, 9.0 mmol of CrO_2F_2 was added. The orange solid product (7.0 mmol of $K_2CrO_2F_4$) was formed at 65-75° (6d) and 100° (2d) in ~100% yield; dec. 242, (nc).

The powder spectrum gave the following d values (in Å) with their respective intensities: 3.33 (s), 2.59 (m), 2.37 (m), 2.17 (m), 2.00 (m).

Anal. Calcd for $K_2CrO_2F_4$: Cr, 21.8; F, 31.9. Found: Cr, 19.8; F, 30.2.

Preparation of $Cs_2CrO_2F_4$

To 13.8 mmol of dried CsF in a ~ 125 ml polyethylene vessel, 19.7 mmol of CrO_2F_2 was added. The yellow-orange solid product (7.04 mmol of $Cs_2CrO_2F_4$) was formed at 50-60° (2.5d) in ~100% yield, melting at 340° with dec. at 500°, (nc).

---

*All polyethylene and teflon vessels were equipped with a Whitney Brass valve and a teflon stirring bar. Constant weight was obtained for all products formed from MF or MF_2 and excess CrO_2F_2 by removing all volatile materials under reduced pressure.

The powder spectrum gave the following d values (in Å) with their respective intensities: 3.04 (vs), 3.13 (vs), 3.33 (m), 5.17 (m).

Anal Calcd for $Cs_2CrO_2F_4$: Cr, 12.2; F, 17.9. Found: Cr, 12.5; F, 17.4.

Reaction of LiF with CrO_2F_2

To 23.1 mmol of LiF in a 50 ml monel vessel equipped with a Whitney Brass valve, 11.6 mmol of CrO_2F_2 was added. After 8d at 80°, essentially all of the CrO_2F_2 was recovered and the residue was a light orange-yellow powder.

Preparation of $MgCrO_2F_4$

To 4.8 mmol of MgF_2 in a ~125 ml polyethylene vessel, 7.0 mmol of CrO_2F_2 and excess C_7F_{16} (30 mmol) was added. The orange solid product (4.8 mmol of $MgCrO_2F_4$) was formed at r.t. (4d) in essentially 100% yield; dec. 280°, (nc).

The powder spectrum gave the following d values (in Å) with their respective intensities: 3.26 (s), 2.23 (s), 2.07 (m), 1.71 (s), 1.63 (m), 1.52 (m), 1.38 (s).

Anal. Calcd for $MgCrO_2F_4$: Cr, 28.3. Found: Cr, 27.1.

Preparation of $CaCrO_2F_4$

To 7.1 mmol of CaF_2 in a ~125 ml Teflon vessel, 9.0 mmol of CrO_2F_2 and excess C_7F_{16} (30 mmol) was added. The orange solid product (7.2 mmol of $CaCrO_2F_4$) was formed at ~30° (2d) in ~100% yield; dec. 184° (nc). The Teflon vessel was highly stained indicating CrO_2F_2 uptake.

The powder spectrum gave the following d values (in Å) with their respective intensities: 3.15 (vs), 1.93 (vs), 1.69 (s).

Anal. Calcd for $CaCrO_2F_4$: F, 38.4. Found: F, 38.0.

Preparation of $CrO_2(SO_3F)_2$

To 20.5 mmol of SO_3 in a fused silica reaction vessel (~ 100 ml) equipped with a Kontes Teflon stopcock and Teflon stirring bar, 4.46 mmol of CrO_2F_2 was added. The light green-brown solid product [4.46 mmol of $CrO_2(SO_3F)_2$] was formed at 25° (3d) and 57° (1d) in 100% yield; dec. 123°.

The x-ray powder spectrum gave the following strong and medium lines (d) values in Å): 7.04 (s), 4.66 (s), 4.38 (s), 3.50 (m), 3.15 (m) which agreed with that previously reported.[11]

Anal. Calcd for $CrO_2(SO_3F)_2$: Cr, 18.4; S, 22.7; F, 13.5. Found: Cr, 18.6; S, 22.5; F, 13.0.

Preparation of $CrO_2F(TaF_6)$

To 6.55 mmol of TaF_5 in a ~ 200 ml fused silica vessel, 7.4 mmol of CrO_2F_2 was added. The orange solid product [6.53 mmol of $CrO_2F(TaF_6)$] was formed at 50-60° (1d) and 90-100° (4d) in essentially 100% yield; dec. 104°, (nc).

The powder spectrum gave the following d values (in Å) with their respective intensities: 4.42 (s), 3.59 (vs), 2.80 (s), 2.30 (s), 2.13 (m) 1.98 (s), 1.79 (s), 1.73 (s), 1.69 (m), 1.56 (m), 1.50 (m), 1.48 (m).

Anal. Calcd for $CrO_2F(TaF_6)$: F, 33.4. Found: F, 33.1.

Preparation of $CrO_2F(Sb_2F_{11})$

To 11.6 mmol of SbF_5 (pretreated with dried NaF) in a ~ 100 ml fused silica reaction vessel equipped with a Kontes Teflon stopcock and Teflon stirring bar, 4.14 mmol of CrO_2F_2 was added. The yellow-brown solid product [3.94 mmol of $CrO_2F(Sb_2F_{11})$] was formed at r.t. (4d in dark) in ~95% yield; m.p. 82-84°, (nc).

The powder spectrum gave the following d values (in Å) with their respective intensities: 4.78 (m), 4.35 (s), 3.17 (m), 3.97 (m), 3.55 (m).

Anal. Calcd for $CrO_2F(Sb_2F_{11})$: F, 41.2. Found: F, 41.0.

Preparation of $CrO_2F(SbF_6)$

To 2.11 mmol of SbF_5 (pretreated with dried NaF) in a ~100 ml fused silica vessel, 4.97 mmol of CrO_2F_2 was added. The brown solid product [2.07 mmol of $CrO_2F(SbF_6)$] was formed at r.t. (4d) in ~ 100% yield; m.p. 93-98° with dec., (nc).

A powder spectrum showed this material to be amorphous.

Anal. Calcd for $CrO_2F(SbF_6)$: F, 39.3. Found: F, 39.0.

Preparation of $CrO_2(CF_3COO)_2$

To 40.2 mmol of $(CF_3CO)_2O$ in a ~50 ml Pyrex glass vessel equipped with a Kontes Teflon stopcock and Teflon stirring bar, 8.38 mmol of CrO_2F_2 was added. Upon warming, a red solution was formed and after 1.6 hr. at r.t. the solution had turned brown. The volatile materials, which contained 19.6 mmol of CF_3COF and unreacted $(CF_3CO)_2O$, were pumped away through a trap cooled to -196° and were identified by their infrared spectra. An infrared spectrum of the brown solid product [7.8 mmol of $CrO_2(CF_3COO)_2$] agreed with that of $CrO_2(CF_3COO)_2$.

AsF_5 with CrO_2F_2

To 8.82 mmol of AsF_5 in a ~ 100 ml silica vessel equipped with a Kontes Teflon stopcock, 2.91 mmol of CrO_2F_2 was added. After 1d at r.t., the materials, volatile at -78°, were removed by pumping through a trap cooled to -196°. The AsF_5 was quantitatively recovered.

PF_5 with CrO_2F_2

To 7.89 mmol of PF_5 in a ~100 ml silica vessel equipped with a Kontes Teflon stopcock, 3.17 mmol of CrO_2F_2 was added. After 1d at r.t., the materials, volatile at -78°, were removed by pumping through a trap cooled to -196°. The PF_5 was quantitatively recovered.

BF_3 with CrO_2F_2

To 2.65 mmol of BF_3 in a ~50 ml pyrex-glass vessel equipped with a Kontes Teflon stopcock, 1.03 mmol of CrO_2F_2 was added. Warming to r.t. resulted in no observable reaction. The volatile materials at -78° were removed by pumping through a trap cooled to -196°. The BF_3 was quantitatively recovered at -78°.

Reaction of NaCl with CrO_2F_2

13.8 mmol of NaCl was placed in a 100 ml polyethylene vessel. 12.3 mmol of CrO_2F_2 was condensed in at -196°, the vessel was warmed to r.t. and the two reactants were stirred for 14 days.

The materials, volatile at r.t., were condensed in a -196° trap. A volatile red liquid at r.t. was present and an i.r. spectrum showed it to be CrO_2Cl_2 [3.23 mmol, yield of 52.7% based on equation (11)]. The nonvolatile solid product $Na_2CrO_2F_4$ was identified by its infrared spectrum and x-ray powder lines.

Reaction of CF_3COONa with CrO_2F_2 in CF_3COOH

To 5.60 mmol of CF_3COONa in a ~60 ml pyrex-glass vessel, 2.79 mmol of CrO_2F_2 and 56.1 mmol of CF_3COOH were added. The red-brown solid product [2.74 mmol of $Na_2CrO_2F_2(CF_3COO)_2$] was formed at r.t. in the dark (4d). CF_3COOH was removed by heating to 60° for 2 hr, m.p. 90-94°, (nc).

Anal. Calcd for $Na_2CrO_2F_2(CF_3COO)_2$: Cr, 13.2; C, 12.2; F, 38.6. Found: Cr, 13.1; C, 12.0; F, 37.9.

Reaction of NO with CrO_2F_2

To 22.3 mmol of purified NO in a ~200 ml silica vessel, 8.32 mmol of CrO_2F_2 was added. Reaction was evident even at -196°. Upon warming to r.t. and removing excess NO, a brown solid product (8.30 mmol of $NO{\cdot}CrO_2F_2$) was present; dec. 63°, (nc).

A powder spectrum of this material showed the solid to be amorphous.

Anal. Calcd for $NO \cdot CrO_2F_2$: Cr, 34.3; N, 9.2; F, 25.0. Found: Cr, 34.0 N, 9.0; F, 24.5

Reaction of SO_2 with CrO_2F_2

To 8.07 mmol of SO_2 in a 200 ml silica vessel, 4.44 mmol of CrO_2F_2 was added. The reaction proceeded for 1d at r.t., after which the excess SO_2 was removed. The yellow-brown solid left behind corresponded to $SO_2 \cdot 2CrO_2F_2$; dec. 150°, (nc). Heating the reactants to 100° for 2 hr in a 30 ml stainless steel Hoke vessel produced the same product in 100% yield.

A powder spectrum showed the material to be amorphous.

Anal. Calcd for $SO_2 \cdot 2CrO_2F_2$: Cr, 33.8; S, 10.4; F, 24.7. Found: Cr, 33.5; S, 10.6; F, 24.1.

ACKNOWLEDGEMENT

We wish gratefully to acknowledge the support of the donors of the Petroleum Research Fund administered by the American Chemical Society. We are also indebted to Professor Tom Loehr and the Oregon Graduate Center for the use of their laser Raman spectrometer.

REFERENCES

1. A. Englebrecht and A.V. Grosse, J. Amer. Chem. Soc., 74, (1952) 5262.
2. O. Unverdorben, Ann. Physik Chem., 7, (1826) 311.
3. O. Unverdorben, Trommsdorff's J., 9, (1824) 26.
4. H. von Wartenberg, Z. Anorg. Allgem. Chem., 247, (1941) 135.
5. G.D. Flesch and H.J. Svec. J. Amer. Chem. Soc., 80, (1958) 3189.
6. J.G. Malm, H. Selig, and S. Siegel, Inorg. Chem., 5, (1966) 130.
7. S.D. Brown and G.L. Gard, Inorg. Chem., 12, (1973) 483.
8. O.H. Wheeler, Can. J. Chem., 38, (1960) 2137.

9. W.P. Griffith, J. Chem. Soc. (A), (1969) 211.

10. R.C. Makhija and R.A. Stairs, Can. J. Chem., 47, (1969) 2293.

11. W.V. Rochat and G.L. Gard, Inorg. Chem., 8, (1969) 158.

12. J.N. Gerlach and G.L. Gard, Inorg. Chem., 9, (1970) 1565.

13. W.E. Hobbs, J. Chem. Phys., 28, (1958) 1220.

14. H. Stammreich, O.Sala, and D. Bassi, Spectrochimica Acta., 19, (1963) 593.

15. H.A. Carter and F. Aubke, Can. J. Chem., 48, (1970) 3456.

16. D.E. McKee and N. Bartlett, Inorg. Chem., 12, (1973) 2738.

17. D.E. McKee, C.J. Adams and N. Bartlett, Inorg. Chem., 12, (1973) 1722.

18. J. S. Fordyce and R. L. Baum, J. Chem. Phys., (1966), 1159.

19. J.N. Gerlach and G.L. Gard, Inorg. Chem., 10, (1971) 1541.

20. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N.Y., 1963. p. 90-94.

21. F.A. Cotton, D.M.L. Goodgame, M. Goodgame, and A. Sacco, J. Amer. Chem. Soc., 83, (1961) 4157.