

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  $\text{CrO}_2\text{F}_2$  with MF or  $\text{MF}_2$  gave the corresponding  $\text{M}_2\text{CrO}_2\text{F}_4$  and  $\text{MCrO}_2\text{F}_4$  fluorochromates. With the Lewis Acids ( $\text{SO}_3$ ,  $\text{TaF}_5$ ,  $\text{SbF}_5$ ) and  $(\text{CF}_3\text{CO})_2\text{O}$  known and new chromyl compounds [ $\text{CrO}_2(\text{CF}_3\text{COO})_2$ ,  $\text{CrO}_2(\text{SO}_3\text{F})_2$ ,  $\text{CrO}_2\text{FTaF}_6$ ,  $\text{CrO}_2\text{FSbF}_6$ ,  $\text{CrO}_2\text{FSb}_2\text{F}_{11}$ ] were produced. Chromyl fluoride and inorganic salts ( $\text{CF}_3\text{COONa}$  and  $\text{NaNO}_3$ ) produced the following complexes -  $\text{Na}_2\text{CrO}_2\text{F}_2(\text{CF}_3\text{COO})_2$  and  $\text{Na}_2\text{CrO}_2\text{F}_2(\text{NO}_3)_2$ . Unusual solid products were obtained with  $\text{CrO}_2\text{F}_2$  and NO,  $\text{NO}_2$ ,  $\text{SO}_2$ .

A new method of preparing  $\text{CrO}_2\text{F}_2$  is also presented.

#### INTRODUCTION

The literature dealing with chromyl compounds covers essentially chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) and its reactions. The fluorine analog of

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\* 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.

$\text{CrO}_2\text{Cl}_2$ , chromyl fluoride ( $\text{CrO}_2\text{F}_2$ ) 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  $\text{CrO}_2\text{F}_2$  was full of conflicting and sketchy information and even today very little information is known about its chemical properties.

Unverdorben [2] found that  $\text{CrO}_2\text{F}_2$  is reduced by arsenic trioxide, forming arsenic fluorides and chromic oxide. Also, he found that  $\text{CrO}_2\text{F}_2$  exchanges its fluorines with numerous metal oxides, forming  $\text{BF}_3$  from boric oxide and  $\text{SiF}_4$  from glass.[3]

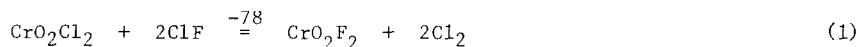
$\text{CrO}_2\text{F}_2$  is described as a strong fluorinating agent.[4] However, this report as well as earlier reports are likely to be erroneous because  $\text{CrO}_2\text{F}_2$  was contaminated with fluorine.

Flesch and Svec [5] produced  $\text{CrO}_2\text{ClF}$  from  $\text{CrO}_2\text{F}_2$  and  $\text{CrO}_2\text{Cl}_2$ . Grosse [1] reported that  $\text{CrO}_2\text{F}_2$  does not react with  $\text{KF}$  or  $\text{NaF}$  at room temperature, but with  $\text{KHF}_2$  and  $\text{NaHF}_2$  produced  $\text{CrO}_2\text{F}_2 \cdot \text{KHF}_2$  and  $\text{CrO}_2\text{F}_2 \cdot \text{NaHF}_2$  complexes.

These studies encompassed all that was known about  $\text{CrO}_2\text{F}_2$  prior to our investigations.

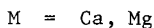
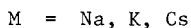
## RESULTS AND DISCUSSION

For most of our studies the  $\text{CrO}_2\text{F}_2$  was prepared by essentially the method of Flesch and Svec.[5] However, an equally direct and perhaps more convenient method is the following:



Large quantities of pure  $\text{CrO}_2\text{F}_2$  have been prepared in this manner.

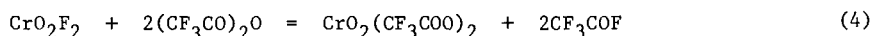
We have found that under proper conditions  $\text{CrO}_2\text{F}_2$  will react with Group IA and Group IIA metal fluorides generally producing orange colored solid fluorochromates in essentially 100% yield according to the following equations:



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]

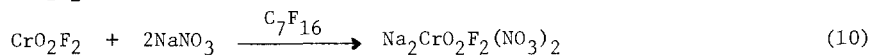
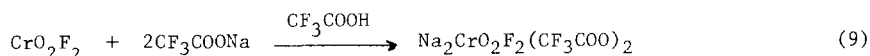
These new compounds fume in moist air and hydrolyze in water giving yellow dichromate solutions. Also, they react with organic compounds producing brownish products that were not investigated.  $LiF$  did not react under comparable conditions.

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

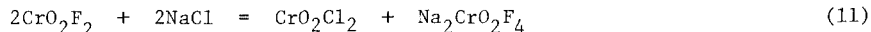


These solid compounds are regarded as chromyl compounds and are quite reactive with water producing yellow dichromate solutions. In the reaction with other weaker Lewis Acids ( $PF_5$ ,  $BF_3$ ,  $AsF_5$ ) no reaction was evident at room temperature.

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:

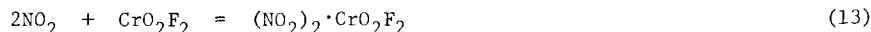


However, with NaCl only  $\text{CrO}_2\text{Cl}_2$  and  $\text{Na}_2\text{CrO}_2\text{F}_4$  were formed at room temperature.



In reference to equation 10, it is interesting that without the solvent  $\text{C}_7\text{F}_{16}$  and with excess  $\text{CrO}_2\text{F}_2$ ,  $\text{CrO}_2(\text{NO}_3)_2$  and  $\text{Na}_2\text{CrO}_2\text{F}_4$  were formed.[7] Therefore, in addition to producing new fluorochromates there is a possibility of forming chromyl compounds from  $\text{CrO}_2\text{F}_2$  and inorganic salts.

Chromyl compounds are powerful oxidizing agents and as such react vigorously with  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{SO}_2$  according to the following equations:



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  $\text{CrO}_2\text{Cl}_2$  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  $(\text{NO}_2)_2 \cdot \text{CrO}_2\text{F}_2$  is in an oxidation state of four while for  $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$  and  $\text{NO} \cdot \text{CrO}_2\text{F}_2$  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 ( $d^0$ ) dioxo complexes possess

TABLE I

Magnetic Susceptibilities  
of Inorganic Chromium Complexes

	Expt'l, $\chi_{\text{eff}}$ (B.M.)*
$\text{NO} \cdot \text{CrO}_2\text{F}_2$	1.79 <sup>‡</sup>
$(\text{NO}_2)_2 \cdot \text{CrO}_2\text{F}_2$	3.12
$\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$	2.73

The theoretical  $\chi_{\text{eff}}$  for  $\text{Cr}^{+4}$  is 2.83 B.M.

<sup>‡</sup> Heating  $\text{NO} \cdot \text{CrO}_2\text{F}_2$  for 16 hrs. at 65° increased the  $\chi_{\text{eff}}$  to 2.91 B.M.  
Evidently the  $\text{NOCrO}_2\text{F}_2$  is slowly converted in part to  $\text{NO}_2\text{CrOF}_2$ .

the cis- and the  $d^2$  transition-metal dioxo complexes the trans dioxo structure. For the octahedral cis-dioxo compounds (symmetry  $C_{2v}$ ) the  $\nu_s(\text{MO}_2)$  and  $\delta(\text{MO}_2)$  are  $A_1$  modes and  $\nu_{\text{as}}(\text{MO}_2)$  is  $B_1$ ; all three are active in the i.r. For the compounds  $\text{Na}_2\text{WO}_2\text{F}_4$  and  $\text{Na}_2\text{MoO}_2\text{F}_4$ ,  $\nu_s(\text{MO}_2)$  and  $\nu_{\text{as}}(\text{MO}_2)$  were found at 951 and 958  $\text{cm}^{-1}$  and 904 and 920  $\text{cm}^{-1}$  respectively.[9] Assuming the fluorochromates (Cr VI,  $d^0$ ) possess the cis-dioxo structure the corresponding sym. and asym.,  $\text{MO}_2$  stretching vibrations should be infrared active and have similar frequencies and intensities. For the alkali metal fluorochromates (see Table II)  $\text{MO}_2$  vibrations and intensities ( $\nu_s$  935-955  $\text{cm}^{-1}$ ;  $\nu_{\text{as}}$  910-915  $\text{cm}^{-1}$ ) similar to  $\text{Na}_2\text{WO}_2\text{F}_4$  and  $\text{Na}_2\text{MoO}_2\text{F}_4$  are found. This result strongly supports a cis-dioxo structure for these salts. There are additional bands similar to the  $\text{O}=\text{Cr}=\text{O}$  vibrations particularly for  $\text{Na}_2\text{CrO}_2\text{F}_4$ ,  $\text{K}_2\text{CrO}_2\text{F}_4$  and  $\text{CaCrO}_2\text{F}_4$ . These may be due to interaction between  $\text{Cr}=\text{O}$  groups in neighboring molecules. Makhija and Stairs came to a similar conclusion for their reported chromyl chloride triphenylphosphine and triphenylarsine complexes.[10] The  $\delta(\text{MO}_2)$  deformation bands for the

TABLE II

Infrared Spectra of  $\text{CrO}_2\text{F}_2$  and Lewis Base Products ( $\text{cm}^{-1}$ )

$\text{Na}_2\text{CrO}_2\text{F}_4$	$\text{K}_2\text{CrO}_2\text{F}_4$	$\text{Cs}_2\text{CrO}_2\text{F}_4$
1200 (m)	1034 (m)	946 (s) with sh.
955 (s)	955 (s)	1000 $\text{cm}^{-1}$
935 (m)	915 (m)	910 (m)
910 (m)	635 (s,b)	631 (s,b)
720 (w)	315 (w,b)	500 (m,b)
580 (s,b)		330 (w)
467 (w)		
380 (w,b)		

$\text{MgCrO}_2\text{F}_2$	$\text{CaCrO}_2\text{F}_4$	$\text{Na}_2\text{CrO}_2(\text{CF}_3\text{COO})_2\text{F}_2$
948 (s)	1230 (w)	1620 (m)
899 (w)	976 (s) with sh	1429 (w)
825 (w)	at 990	1350 (w)
740 (m,b)	968 (s) with sh.	1160 (s)
450 (s,b)	at 940	935 (m)
400 (s)	890 (w-m)	844 (w)
	825 (m,b)	807 (w)
	470-300 (s,b)	704 (w,b)

$\text{Na}_2\text{CrO}_2(\text{NO}_3)_2\text{F}_2^\ddagger$
1630 (w)
1350 (s)
963 (m,b)
899 (w)
875 (w)
833 (m)

 $^\ddagger$  See ref. 7 for preparation of this compound.

alkali metal fluorochromates are found in the  $315\text{--}380\text{ cm}^{-1}$  region. For  $\text{Na}_2\text{WO}_2\text{F}_4$  and  $\text{Na}_2\text{MoO}_2\text{F}_4$ , the  $\delta(\text{MO}_2)$  deformation bands are found at  $378\text{ cm}^{-1}$  and  $385\text{ cm}^{-1}$ , 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  $\text{CrO}_2(\text{SO}_3\text{F})_2$  and  $\text{CrO}_2(\text{CF}_3\text{COO})_2$  agreed with previously reported values.[11,12] For  $\text{CrO}_2\text{F}_2 \cdot \text{SbF}_5$  and  $\text{CrO}_2\text{F}_2 \cdot 2\text{SbF}_5$  the sym.  $[\nu_s(\text{MO}_2)]$  metal-oxygen vibrations are located at  $950$  and  $940\text{ cm}^{-1}$ . The asym.  $[\nu_{as}(\text{MO}_2)]$  metal-oxygen vibrations are

found at 970 and 955  $\text{cm}^{-1}$ . By comparison,  $\text{CrO}_2\text{F}_2$  sym. and asym. metal-oxygen vibrations are at 1006 and 1017  $\text{cm}^{-1}$ , [13] while in  $\text{KCrO}_3\text{F}$  they are found at 912 and 952  $\text{cm}^{-1}$ . [14]

The Raman spectra for  $\text{CrO}_2\text{F}_2 \cdot \text{SbF}_5$  and  $\text{CrO}_2\text{F}_2 \cdot 2\text{SbF}_5$  were obtained under instrumental conditions of low sensitivity over a range of 300-1200  $\text{cm}^{-1}$ . The observed frequencies ( $\text{cm}^{-1}$ ) and relative intensities for  $\text{CrO}_2\text{F}_2 \cdot \text{SbF}_5$  are located at 663 (s), 940 (m), 960 (s) and for  $\text{CrO}_2\text{F}_2 \cdot 2\text{SbF}_5$  are at 660 (s), 697 (m-s) and 945 (s). For the  $\text{CrO}_2\text{F}_2 \cdot \text{SbF}_5$  complex the Raman line at 663  $\text{cm}^{-1}$  is characteristic for the  $\text{SbF}_6^-$  ion. In  $\text{KSbF}_6$  [15] and  $\text{O}_2\text{SbF}_6$  [16] the Raman lines are located at 661  $\text{cm}^{-1}$  and 656  $\text{cm}^{-1}$ , respectively. The 940  $\text{cm}^{-1}$  and 960  $\text{cm}^{-1}$  lines are due to Cr-O stretching frequencies.

For the  $\text{CrO}_2\text{F}_2 \cdot 2\text{SbF}_5$  complex the Raman lines at 660  $\text{cm}^{-1}$  and 697  $\text{cm}^{-1}$  are characteristic of the  $\text{Sb}_2\text{F}_{11}^-$  ion. In  $\text{KrFSb}_2\text{F}_{11}$  [17] these Raman lines are located at 693  $\text{cm}^{-1}$  and 679  $\text{cm}^{-1}$ , while for  $\text{O}_2\text{Sb}_2\text{F}_{11}$  [16] they are found at 688  $\text{cm}^{-1}$  and 659  $\text{cm}^{-1}$ . The 945  $\text{cm}^{-1}$  absorption is attributable to the Cr-O stretching mode.

The Raman results strongly suggest that for the 1:1 and 1:2 complexes,  $\text{SbF}_6^-$  and  $\text{Sb}_2\text{F}_{11}^-$  anions are present, respectively. The cation characteris-

TABLE III

Lewis Acid Products ( $\text{cm}^{-1}$ ) Infrared Spectra of  $\text{CrO}_2\text{F}_2$  and

$\text{CrO}_2\text{F}(\text{SbF}_6)$	$\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})$	$\text{CrO}_2\text{F}(\text{TaF}_6)$
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)	
	460 (m)	
477 (m)	304 (m)	
375 (w-m)		
304 (m)		

TABLE IV

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

$\text{NO} \cdot \text{CrO}_2\text{F}_2$	$(\text{NO}_2)_2\text{CrO}_2\text{F}_2$ †	$\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$
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  $\text{CrO}_2\text{F}^+$ . This interpretation would not rule out fluorine bridge bonding between Cr and Sb thereby increasing the coordination number around Cr to four.

For  $\text{CrO}_2\text{F}_2 \cdot \text{TaF}_5$  the sym. and asym. metal-oxygen vibrations are at 895 and  $934 \text{ cm}^{-1}$ , respectively. The strong band centered at  $573 \text{ cm}^{-1}$  is probably the Ta-F stretching vibration which is located at  $582 \text{ cm}^{-1}$  in the  $\text{TaF}_6^-$  ion.[18] This evidence favors the formulation of  $\text{CrO}_2\text{F}_2 \cdot \text{TaF}_5$  as  $\text{CrO}_2\text{F}^+\text{TaF}_6^-$ .

The infrared spectrum of  $\text{Na}_2\text{CrO}_2\text{F}_2(\text{CF}_3\text{COO})_2$  given in Table II shows the COO asymmetric stretch at  $1620 \text{ cm}^{-1}$  while the COO symmetric stretch is probably at  $1350 \text{ cm}^{-1}$ . The C-F asymmetric stretch occurs at  $1160 \text{ cm}^{-1}$  with the  $\text{CF}_3$  symmetric stretch at  $807 \text{ cm}^{-1}$ . The absorption band at  $844 \text{ cm}^{-1}$  is the C-C stretch and the one at  $704 \text{ cm}^{-1}$  the  $\text{CCO}_2$  in-plane bend. The  $935 \text{ cm}^{-1}$  band represents the Cr-O stretch. The infrared spectrum and assignments of  $\text{Na}_2\text{CrO}_2\text{F}_2(\text{CF}_3\text{COO})_2$  are very similar to other oxochromium trifluoroacetate salts [i.e.  $\text{K}_2\text{CrO}_2(\text{CF}_3\text{COO})_4$ ] previously reported.[19]

For  $\text{Na}_2\text{CrO}_2\text{F}_2(\text{NO}_3)_2$  in Table II, the absorption band at  $1350 \text{ cm}^{-1}$  is probably the asymmetric N-O stretching vibration and the absorption band at



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

The broad absorption bands for  $(\text{NO}_2)_2\text{CrO}_2\text{F}_2$ ,  $\text{NO}\cdot\text{CrO}_2\text{F}_2$ , and  $\text{SO}_2\cdot 2\text{CrO}_2\text{F}_2$  at 955  $\text{cm}^{-1}$ , 980  $\text{cm}^{-1}$ , and 974  $\text{cm}^{-1}$  respectively represent the Cr-O stretching vibrations. Although additional tentative assignments can be made for these complexes [e.g. the absorption bands at 2360  $\text{cm}^{-1}$  and 550  $\text{cm}^{-1}$  in  $(\text{NO}_2)_2\text{CrO}_2\text{F}_2$  are attributable to  $\text{NO}_2^+$  and the absorption bands at 1485  $\text{cm}^{-1}$  and 1265  $\text{cm}^{-1}$  are attributable to bridging  $\text{NO}_2$  groups; the absorption band for  $\text{NO}\cdot\text{CrO}_2\text{F}_2$  at 2280  $\text{cm}^{-1}$  is attributable to  $\text{NO}^+$ ; for the  $\text{SO}_2\cdot\text{CrO}_2\text{F}_2$  complex the absorption bands at 1130  $\text{cm}^{-1}$  and 1050  $\text{cm}^{-1}$  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,  $\text{CaF}_2$  and  $\text{NaNO}_3$  used in this study were obtained from Mallinckrodt and were reagent grade. They were thoroughly dried immediately before use.  $\text{PF}_5$ , CsF,  $\text{CF}_3\text{COONa}$ ,  $\text{TaF}_5$ , and  $\text{C}_7\text{F}_{16}$  were purchased from Penninsular Chem Research and were of 98% purity; the CsF was dried before use.  $\text{CrO}_2\text{Cl}_2$ ,  $\text{MgF}_2$ , and KF were obtained from Alpha Inorganic Chemicals. The  $\text{MgF}_2$  and KF were dried thoroughly before use; the  $\text{CrO}_2\text{Cl}_2$  was distilled from Hg.  $\text{SO}_3$  was obtained from J. Baker Chemicals and was vacuum distilled before use. The  $\text{BF}_3$ ,  $\text{NO}_2$ , and  $\text{SO}_2$  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<sub>2</sub> 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<sub>2</sub>F<sub>2</sub>·SbF<sub>5</sub> and CrO<sub>2</sub>F<sub>2</sub>·2SbF<sub>5</sub> were contained as solids in 5-mm o.d. "optically flat" pyrex cells at room temperature. The spectral slit width was 12 cm<sup>-1</sup>.

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 (~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<sub>4</sub>·5H<sub>2</sub>O 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 CuKα radiation was used. The procedure was standardized using known compounds (CrO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, CrF<sub>3</sub>·H<sub>2</sub>O) 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 phenolphthalein indicator. Standard analyses were performed by Beller Laboratories, Göttingen, West Germany.

#### Preparation of $\text{CrO}_2\text{F}_2$

To 31.0 mmol of  $\text{CrO}_2\text{Cl}_2$  in a 30 ml Hoke vessel equipped with an Autoclave spacesaver valve, 64.0 mmol of  $\text{ClF}$  was added. The reactant materials were kept at  $-78^\circ$  for 24 hr. The volatile materials ( $\text{Cl}_2$  and  $\text{ClF}$ ) were pumped away at  $-78^\circ$ . The  $\text{CrO}_2\text{F}_2$  (30.6 mmol) was formed in essentially 100% yield.

The infrared spectrum agreed with the literature.[13]

Anal. Calcd for  $\text{CrO}_2\text{F}_2$ : Cr, 42.6. Found: Cr, 42.7 via iodometry, 42.3 via acidity.

#### Preparation of $\text{K}_2\text{CrO}_2\text{F}_4$ \*

To 13.9 mmol of dried  $\text{KF}$  in a  $\sim 125$  ml polyethylene vessel, 9.0 mmol of  $\text{CrO}_2\text{F}_2$  was added. The orange solid product (7.0 mmol of  $\text{K}_2\text{CrO}_2\text{F}_4$ ) was formed at  $65-75^\circ$  (6d) and  $100^\circ$  (2d) in  $\sim 100\%$  yield; dec.  $242^\circ$ , (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  $\text{K}_2\text{CrO}_2\text{F}_4$ : Cr, 21.8; F, 31.9. Found: Cr, 19.8; F, 30.2.

#### Preparation of $\text{Cs}_2\text{CrO}_2\text{F}_4$

To 13.8 mmol of dried  $\text{CsF}$  in a  $\sim 125$  ml polyethylene vessel, 19.7 mmol of  $\text{CrO}_2\text{F}_2$  was added. The yellow-orange solid product (7.04 mmol of  $\text{Cs}_2\text{CrO}_2\text{F}_4$ ) was formed at  $50-60^\circ$  (2.5d) in  $\sim 100\%$  yield, melting at  $340^\circ$  with dec. at  $500^\circ$ , (nc).

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\*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  $\text{MF}$  or  $\text{MF}_2$  and excess  $\text{CrO}_2\text{F}_2$  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  $\text{Cs}_2\text{CrO}_2\text{F}_4$ : Cr, 12.2; F, 17.9. Found: Cr, 12.5; F, 17.4.

#### Reaction of LiF with $\text{CrO}_2\text{F}_2$

To 23.1 mmol of LiF in a 50 ml monel vessel equipped with a Whitney Brass valve, 11.6 mmol of  $\text{CrO}_2\text{F}_2$  was added. After 8d at 80°, essentially all of the  $\text{CrO}_2\text{F}_2$  was recovered and the residue was a light orange-yellow powder.

#### Preparation of $\text{MgCrO}_2\text{F}_4$

To 4.8 mmol of  $\text{MgF}_2$  in a ~125 ml polyethylene vessel, 7.0 mmol of  $\text{CrO}_2\text{F}_2$  and excess  $\text{C}_7\text{F}_{16}$  (30 mmol) was added. The orange solid product (4.8 mmol of  $\text{MgCrO}_2\text{F}_4$ ) 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  $\text{MgCrO}_2\text{F}_4$ : Cr, 28.3. Found: Cr, 27.1.

#### Preparation of $\text{CaCrO}_2\text{F}_4$

To 7.1 mmol of  $\text{CaF}_2$  in a ~125 ml Teflon vessel, 9.0 mmol of  $\text{CrO}_2\text{F}_2$  and excess  $\text{C}_7\text{F}_{16}$  (30 mmol) was added. The orange solid product (7.2 mmol of  $\text{CaCrO}_2\text{F}_4$ ) was formed at ~30° (2d) in ~100% yield; dec. 184° (nc). The Teflon vessel was highly stained indicating  $\text{CrO}_2\text{F}_2$  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  $\text{CaCrO}_2\text{F}_4$ : F, 38.4. Found: F, 38.0.

### Preparation of $\text{CrO}_2(\text{SO}_3\text{F})_2$

To 20.5 mmol of  $\text{SO}_3$  in a fused silica reaction vessel ( $\sim 100$  ml) equipped with a Kontes Teflon stopcock and Teflon stirring bar, 4.46 mmol of  $\text{CrO}_2\text{F}_2$  was added. The light green-brown solid product [4.46 mmol of  $\text{CrO}_2(\text{SO}_3\text{F})_2$ ] was formed at  $25^\circ$  (3d) and  $57^\circ$  (1d) in 100% yield; dec.  $123^\circ$ .

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  $\text{CrO}_2(\text{SO}_3\text{F})_2$ : Cr, 18.4; S, 22.7; F, 13.5. Found: Cr, 18.6; S, 22.5; F, 13.0.

### Preparation of $\text{CrO}_2\text{F}(\text{TaF}_6)$

To 6.55 mmol of  $\text{TaF}_5$  in a  $\sim 200$  ml fused silica vessel, 7.4 mmol of  $\text{CrO}_2\text{F}_2$  was added. The orange solid product [6.53 mmol of  $\text{CrO}_2\text{F}(\text{TaF}_6)$ ] was formed at  $50-60^\circ$  (1d) and  $90-100^\circ$  (4d) in essentially 100% yield; dec.  $104^\circ$ , (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  $\text{CrO}_2\text{F}(\text{TaF}_6)$ : F, 33.4. Found: F, 33.1.

### Preparation of $\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})$

To 11.6 mmol of  $\text{SbF}_5$  (pretreated with dried NaF) in a  $\sim 100$  ml fused silica reaction vessel equipped with a Kontes Teflon stopcock and Teflon stirring bar, 4.14 mmol of  $\text{CrO}_2\text{F}_2$  was added. The yellow-brown solid product [3.94 mmol of  $\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})$ ] was formed at r.t. (4d in dark) in  $\sim 95\%$  yield; m.p.  $82-84^\circ$ , (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  $\text{CrO}_2\text{F}(\text{Sb}_2\text{F}_{11})$ : F, 41.2. Found: F, 41.0.

Preparation of  $\text{CrO}_2\text{F}(\text{SbF}_6)$ 

To 2.11 mmol of  $\text{SbF}_5$  (pretreated with dried NaF) in a  $\sim 100$  ml fused silica vessel, 4.97 mmol of  $\text{CrO}_2\text{F}_2$  was added. The brown solid product [ $2.07$  mmol of  $\text{CrO}_2\text{F}(\text{SbF}_6)$ ] was formed at r.t. (4d) in  $\sim 100\%$  yield; m.p.  $93-98^\circ$  with dec., (nc).

A powder spectrum showed this material to be amorphous.

Anal. Calcd for  $\text{CrO}_2\text{F}(\text{SbF}_6)$ : F, 39.3. Found: F, 39.0.

Preparation of  $\text{CrO}_2(\text{CF}_3\text{COO})_2$ 

To 40.2 mmol of  $(\text{CF}_3\text{CO})_2\text{O}$  in a  $\sim 50$  ml Pyrex glass vessel equipped with a Kontes Teflon stopcock and Teflon stirring bar, 8.38 mmol of  $\text{CrO}_2\text{F}_2$  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  $\text{CF}_3\text{COF}$  and unreacted  $(\text{CF}_3\text{CO})_2\text{O}$ , were pumped away through a trap cooled to  $-196^\circ$  and were identified by their infrared spectra. An infrared spectrum of the brown solid product [ $7.8$  mmol of  $\text{CrO}_2(\text{CF}_3\text{COO})_2$ ] agreed with that of  $\text{CrO}_2(\text{CF}_3\text{COO})_2$ .

 $\text{AsF}_5$  with  $\text{CrO}_2\text{F}_2$ 

To 8.82 mmol of  $\text{AsF}_5$  in a  $\sim 100$  ml silica vessel equipped with a Kontes Teflon stopcock, 2.91 mmol of  $\text{CrO}_2\text{F}_2$  was added. After 1d at r.t., the materials, volatile at  $-78^\circ$ , were removed by pumping through a trap cooled to  $-196^\circ$ . The  $\text{AsF}_5$  was quantitatively recovered.

 $\text{PF}_5$  with  $\text{CrO}_2\text{F}_2$ 

To 7.89 mmol of  $\text{PF}_5$  in a  $\sim 100$  ml silica vessel equipped with a Kontes Teflon stopcock, 3.17 mmol of  $\text{CrO}_2\text{F}_2$  was added. After 1d at r.t., the materials, volatile at  $-78^\circ$ , were removed by pumping through a trap cooled to  $-196^\circ$ . The  $\text{PF}_5$  was quantitatively recovered.

BF<sub>3</sub> with CrO<sub>2</sub>F<sub>2</sub>

To 2.65 mmol of BF<sub>3</sub> in a ~50 ml pyrex-glass vessel equipped with a Kontes Teflon stopcock, 1.03 mmol of CrO<sub>2</sub>F<sub>2</sub> 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<sub>3</sub> was quantitatively recovered at -78°.

Reaction of NaCl with CrO<sub>2</sub>F<sub>2</sub>

13.8 mmol of NaCl was placed in a 100 ml polyethylene vessel. 12.3 mmol of CrO<sub>2</sub>F<sub>2</sub> 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<sub>2</sub>Cl<sub>2</sub> [3.23 mmol, yield of 52.7% based on equation (11)]. The nonvolatile solid product Na<sub>2</sub>CrO<sub>2</sub>F<sub>4</sub> was identified by its infrared spectrum and x-ray powder lines.

Reaction of CF<sub>3</sub>COONa with CrO<sub>2</sub>F<sub>2</sub> in CF<sub>3</sub>COOH

To 5.60 mmol of CF<sub>3</sub>COONa in a ~60 ml pyrex-glass vessel, 2.79 mmol of CrO<sub>2</sub>F<sub>2</sub> and 56.1 mmol of CF<sub>3</sub>COOH were added. The red-brown solid product [2.74 mmol of Na<sub>2</sub>CrO<sub>2</sub>F<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub>] was formed at r.t. in the dark (4d). CF<sub>3</sub>COOH was removed by heating to 60° for 2 hr, m.p. 90-94°, (nc).

Anal. Calcd for Na<sub>2</sub>CrO<sub>2</sub>F<sub>2</sub>(CF<sub>3</sub>COO)<sub>2</sub>: Cr, 13.2; C, 12.2; F, 38.6.  
Found: Cr, 13.1; C, 12.0; F, 37.9.

Reaction of NO with CrO<sub>2</sub>F<sub>2</sub>

To 22.3 mmol of purified NO in a ~200 ml silica vessel, 8.32 mmol of CrO<sub>2</sub>F<sub>2</sub> 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·CrO<sub>2</sub>F<sub>2</sub>) was present; dec. 63°, (nc).

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

Anal. Calcd for  $\text{NO} \cdot \text{CrO}_2\text{F}_2$ : Cr, 34.3; N, 9.2; F, 25.0. Found: Cr, 34.0  
N, 9.0; F, 24.5

#### Reaction of $\text{SO}_2$ with $\text{CrO}_2\text{F}_2$

To 8.07 mmol of  $\text{SO}_2$  in a 200 ml silica vessel, 4.44 mmol of  $\text{CrO}_2\text{F}_2$  was added. The reaction proceeded for 1d at r.t., after which the excess  $\text{SO}_2$  was removed. The yellow-brown solid left behind corresponded to  $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$ ; dec.  $150^\circ$ , (nc). Heating the reactants to  $100^\circ$  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  $\text{SO}_2 \cdot 2\text{CrO}_2\text{F}_2$ : 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.

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