CO groups is significantly smaller than that of the axial ligands. The equatorial rate constant could not be calculated with any greater certainty than ±50%, and this precluded the evaluation of activation parameters for the equatorial exchange.[13] However, within this limit of accuracy, the rate constants for exchange at the axial positions exceed the equatorial rate constants by a factor of approximately 4.

On the basis of the observed first-order rate law and the activation parameters for exchange of the axial CO groups, it is concluded that exchange at both the equatorial and axial positions occurs by a dissociative mechanism. The possibility of a mechanism involving opening of the chelate ring was recognized, but such a mechanism is not consistent with the observed zero order of the reaction with respect to CO concentration. Moreover, no $Cr(CO)_6$ was detected during the course of the reaction.

The difference in the axial and equatorial rate constants is insufficiently large to allow an unequivocal interpretation of the energy differences involved. However, on the assumption that the ΔS^* term is similar for exchange at axial and equatorial positions, the larger rate constant for the axial exchange reaction may be related to a smaller chromium–carbon bond energy.

The σ-bonding effect of the *o*-phenanthroline on the CO groups is expected to be largely isotropic. This is confirmed by the fact that both the axial and the equatorial CO groups undergo exchange more readily in the *o*-phenanthroline-substituted compound compared with the parent hexacarbonyl.[14] Such a *trans* effect due to σ bonding as may exist for the amine ligand would lead to labilization of the equatorial CO groups over the axial ligands, in direct contrast to the observed results. The explanation of the different rate constants would appear to lie in the fact that the π^* orbitals of the axial CO groups compete for the same set of metal d orbitals, whereas the equatorial CO groups are *trans* to an essentially non-π-bonding ligand. Hence, the Cr–CO bonding to the equatorial CO groups is expected to have a greater degree of π character. This is in accord with the infrared spectrum of the compound, in which the symmetric and asymmetric C–O stretching vibrations occur at higher frequencies for the axial than for the equatorial CO groups.

These results are in accord with the data provided by the recent studies of carbon monoxide exchange with $Mn(CO)_5X$,[3,4] which showed the similarity of exchange rates of CO groups *trans* and *cis* to a halide ligand. In this case, more accurate techniques may be required to detect what is now expected to be only a small difference in the rate of exchange of axial and equatorial CO groups.

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(13) The low solubility of carbon monoxide in the solvent, combined with the factor that there are four unlabeled CO groups on each molecule which can be released by exchange with the free $C^{18}O$, makes more accurate determination of the equatorial rate constants very difficult. The apparent equilibrium distribution of the labeled molecule throughout the various species is defined by

$$4C_0\frac{(4a+b-d)^4}{4a+b} + \frac{4C_1}{2}\frac{(4a+b-d)^3}{4a+b}\frac{d}{4a+b}$$

For a typical run, only 25% of the starting complex was converted to labeled species.

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The Stability of Chromyl Fluoride

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Little is known about the stability of chromyl fluoride. von Wartenberg[2] first studied its stability toward heat and light and more recently Englebrecht and Grosse[3] found CrO_2F_2 to polymerize with light. von Wartenberg found CrO_2F_2 to polymerize readily with ultraviolet irradiation. The polymer was described as being dirty white and melting around 200°. No data seem to be available on the thermal stability of CrO_2F_2.

Results and Discussion

CrO_2F_2 when heated to 500° decomposed quantitatively according to the equation

$$CrO_2F_2 \xrightarrow{500-525^\circ} CrOF_2 + 0.5O_2 \qquad (1)$$

Chromium oxide difluoride ($CrOF_2$) is a brown-black solid (brown when in a finely divided state) and is insoluble in water, in acids (HCl, HF, HNO_3), in bases (NH_4OH, NaOH, KOH), and in common organic solvents. $CrOF_2$ is stable at ~1600° *in vacuo*, but in a nickel crucible at atmospheric pressure and at ~1600° it is converted to Cr_2O_3 and presumably NiF_2.

Table I
Powder Spectrum for $CrOF_2$

d, Å	Intensity	*d*, Å	Intensity	*d*, Å	Intensity
6.32	s	2.27	w	1.760	vw
5.84	s	2.11	vw	1.745	vw
3.75	s	2.07	vw	1.713	w
3.66	m	2.01	vw	1.620	w
3.24	vw	1.984	vw	1.587	w
3.17	vs	1.949	w	1.546	vw
3.06	w	1.882	w	1.528	w
2.93	w	1.831	m	1.458	w
2.42	vw	1.791	w	1.417	w
2.30	w				

The X-ray powder photograph (see Table I for *d* spacings) did not correspond to CrO, CrO_2, Cr_2O_3, Cr_3O_4, Cr_2O_5, Cr_3O_8, CrF_3, CrF_2, $CrF_3\cdot3H_2O$, FeF_2,

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[1] To whom correspondence should be addressed.

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Fe_2F_5, FeF_3, NiF_2, and $NiF_2 \cdot 4H_2O$, which are possible decomposition and reaction products.

The magnetic susceptibility of $CrOF_2$ is 1.1 BM. This value is noticeably lower than that calculated for a Cr(IV) state (theoretical: 2.8 BM) and presumably is caused by the $CrOF_2$ not being magnetically dilute. Other transition metal oxides[4] and fluorides[5] with a probable d^2 configuration for the metal constituent show this magnetic effect.

The stability of the oxides of chromium has been studied[6] and it was found that CrO_3 at 441° under oxygen pressure (25 psi) was converted to Cr_3O_8 while CrO_2 at 545° under oxygen pressure (900 psi) was slowly converted to Cr_2O_3. *In vacuo*, however, CrO_3 and CrO_2 are less stable.[6] Below 360°, CrO_3 decomposes giving Cr_3O_8, Cr_2O_5, and CrO_2, and at 360–460°, the main product is Cr_2O_3 with small amounts of CrO_2. From these results it appears that $CrOF_2$ is more stable than CrO_2.

Among the known chromyl compounds, CrO_2F_2 has the greatest thermal stability as no appreciable decomposition was observed at ~400°. CrO_2Cl_2 decomposes at ~180°[7] while the other chromyl compounds are unstable around room temperature [$CrO_2(NO_3)_2$ undergoes slow decomposition at room temperature[7] and CrO_2Br_2 decomposes below room temperature[8]].

The ultraviolet decomposition of CrO_2F_2 was studied in a fused-silica vessel. The products of all runs were a brown solid, O_2, and SiF_4. In the presence of sunlight at room temperature, only a very small amount of polymer was formed during a 6-hr period. The material was a light yellow-brown solid that appeared to be "dirty white" with CrO_2F_2 present. With ultraviolet irradiation at room temperature in 1 hr, however, the amount of polymer increased fourfold. With warming (~90°) and ultraviolet irradiation for 1.25 hr, the yield increased eightfold. Analyses of these and other samples gave an empirical composition CrO_xF_y where $x = 1.6–2.0$ and $y = 1.4–1.6$. For long irradiation time (greater than 1 hr), it appears that the following reaction occurs

$$CrO_2F_2 + 1.15SiO_2 \xrightarrow[\text{uv, 90°}]{\text{1 hr}} CrO_{1.6}F_{1.4} + 0.35O_2 + 0.15SiF_4 \qquad (2)$$

Shorter irradiation time (less than 1 hr) results in less loss of oxygen from the chromyl group. An infrared spectrum of the solid formed in (2) showed weak but broad Cr=O stretching vibration in the 960–1000-cm^{-1} region. This absorption is in the region for Cr=O stretching vibrations as found by Hobbs[9] for CrO_2F_2 and CrO_2Cl_2, and Rochat and Gard[10] for $CrO_2(SO_3F)_2$. Also, the product of (2) is amorphous (no lines were observed in a powder spectrum), dissolves in excess base forming a green Cr(III) precipitate and a Cr(VI) solution, and is stable up to ~300° in silica. Above 500°, O_2, SiF_4, and $CrOF_2$ are produced.

Experimental Section

1. **Chemicals and Equipment.**—CrO_2F_2 was prepared by essentially the method of Flesch and Svec.[11] Instead of pumping away the CrO_2F_2 *in vacuo*, a slow stream of nitrogen swept away the CrO_2F_2. Using this method it was found that even at ~100°, CrO_2F_2 was being formed and that at 450° (3 hr later), the reaction was complete. The infrared spectrum agreed with the literature.[9] Any HF present was removed by contacting the CrO_2F_2 with dried NaF.

The infrared spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer.

X-Ray powder spectra were obtained using an XRD-5 General Electric camera. Nickel-filtered copper radiation (Cu $K\alpha$) was used. The procedure was standardized using known compounds (CrO_3, Cr_2O_3, $CrF_3 \cdot 3H_2O$) in which the calculated *d* values agreed with the published ASTM values.

2. **Magnetic Susceptibility.**—The Gouy method was used. 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) tetrathiocyanatocobaltate(II), was calculated using the data cited by Cotton, *et al.*[12] Diamagnetic corrections were made using Pascal's constants[13] for oxygen and fluorine.

3. **Preparation of $CrOF_2$.**—CrO_2F_2 was transferred into a Hoke stainless steel cylinder ($V = 75$ ml) equipped with an Autoclave Monel space-saver valve. After heating at 500–525°, the reaction vessel was quenched in cold water and then cooled to −195.8° where the volatiles were pumped away. In a typical run, 3.9×10^{-2} mol of CrO_2F_2 gave 3.9×10^{-2} mol of $CrOF_2$ and 1.9×10^{-2} mol of O_2 (calcd for O_2: 1.9×10^{-2} mol). *Anal.*[14] Calcd for $CrOF_2$: Cr, 49.0; F, 35.9. Found: Cr, 50.0; F, 35.1. A molecular weight determination of the volatile materials at −195° gave a value of 32.0 (calcd: 32).

4. **Preparation of the Polymer CrO_xF_y, $x = 1.6–2.0$, $y = 1.4–1.6$.**—CrO_2F_2 was transferred to a previously dried 250-ml silica vessel equipped with a Kontes Teflon valve. The reaction vessel and 100-W Hanau uv lamp were placed inside a metal container ($V = 3.5$ l.), the light source being about 3 cm from the reaction vessel. During irradiation the silica vessel was rotated every 15 min in order to expose a new silica surface as a brown polymer coated the walls nearest the lamp.

In a typical run, 3.23×10^{-3} mol of CrO_2F_2 was transferred into the silica reaction vessel. The vessel was irradiated for 1.25 hr at ~90°. The reaction vessel was cooled to −195.8° and the volatile materials of mol wt 31 (calcd for O_2: 32) were pumped away. At −78°, an infrared spectrum showed SiF_4 present (some carbon fluorides were also detected). The volatile materials at room temperature were pumped away leaving a brown solid (0.1246 g). *Anal.* Found for the brown solid:[14] Cr, 50.2; F, 24.8. Assuming that the only other element is oxygen, then an empirical formula $CrO_{1.6}F_{1.4}$ is found. The amount of O_2 produced and the oxidizing capacity support this composition. For irradiation time less than 1 hr, analyses[14] of the brown solid gave 45% Cr and 26.5% F (empirical formula is $CrO_2F_{1.5}$). Apparently, the polymer is slowly decomposed by prolonged ultraviolet exposure.

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