New Preparations of Chromium Oxide Tetrafluoride and Chromium Dioxide Difluoride

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CrO_2F_2 and $CrOF_4$ are conveniently prepared from CrO_3 by direct fluorination in a static thermal system, the product depending on the reaction temperature. The vapour pressure of $CrOF_4$ has been measured by a static method, using a diaphragm gauge of high sensitivity, and physical constants and thermodynamic data have been derived from the vapour pressure measurements.

NUMEROUS reports [1-6] have appeared on the preparation of chromium dioxide difluoride. The majority of the preparations involve the reaction of chromium trioxide with a fluorinating agent, such as HF, IF_5, or SF_4; all present some difficulties in the separation and purification of the product.

The only preparation of chromium oxide tetrafluoride previously reported [7] involved the fluorination of chromium metal, the oxide tetrafluoride resulting as a by-product in the preparation of chromium pentafluoride.

The interaction of chromium trioxide with elemental fluorine has not previously been reported. This is a convenient preparative route to both the dioxide difluoride and the oxide tetrafluoride, the particular product depending on the reaction temperature.

EXPERIMENTAL

Preparations.—Chromium trioxide (2 g; Fisher, certified A.C.S. grade) was loaded into a 250 ml Monel reactor in a dry-box. After evacuation of the reactor, fluorine (Matheson, 99% min.) was added to a pressure of 4 atm. The reactor was heated to the appropriate temperature (controlled to within ±5 °C) while the lid was cooled with water. After the reaction, the excess of fluorine was removed at −196°. The volatile products were then distilled at 25° and collected in a Kel-F trap, held at −196°, and subsequently analysed mass spectrometrically. The reactor was then closed off from the vacuum line and removed to the dry-box for inspection. Any solid products were loaded into a mass spectrometer effusion source for examination. The molecular beam mass spectrometer used in this work has been described previously.[8]

When the reaction was carried out at 150 °C for 41 h, all the product was volatile at 25° and rapidly collected in the cooled Kel-F trap. The mass spectrometric cracking pattern was in good agreement with that reported previously [9] for CrO_2F_2 (Table 1). No impurities were detected by the mass spectroscopic examination, and the conversion was quantitative.

When the reaction temperature was increased to 220 °C and the time to 70 h, only a little CrO_2F_2 was formed. This was removed by pumping at −23 °C (CCl_4 slush), collected in a Kel-F trap, and characterised mass spectrometrically as before. When the reactor was warmed to 25°, a crimson product collected in the cooled Kel-F trap more slowly than the CrO_2F_2 sample. Mass spectrometric examination showed this to be chromium oxide tetrafluoride (Table 1). When the reactor was opened in the dry-box, all the CrO_3 had been consumed and a crimson crystalline deposit was found on the cooled lid. The mass spectrum of this solid was identical with that of the oxide tetrafluoride. The effect of varying the reaction time on the yield of $CrOF_4$ was not investigated.

At higher reaction temperatures (250° for 40 h) the yield of $CrOF_4$ was greatly reduced, and when the reactor was opened in the dry-box, a sticky red deposit was found on the cooled lid. The mass spectrum of this material (heated effusion source) showed a cracking pattern characteristic of CrF_5 at lower temperatures, changing to that of CrF_4 as the temperature was raised (Table 1).

Vapour Pressure Measurements.—These were made over the temperature range 0—70 °C in Pyrex glass apparatus, using a diaphragm gauge of high sensitivity as a null instrument. The apparatus and technique have been described previously.[10] After removal of CrO_2F_2, the sample for measurement was slowly sublimed from a trap at 0 °C.

RESULTS AND DISCUSSION

The fluorination of chromium trioxide appears to proceed by stepwise replacement of oxygen by fluorine atoms. Thus at lower temperatures one oxygen atom is replaced to give the dioxide difluoride. Replacement of a second oxygen atom to give the oxide tetrafluoride occurs at intermediate temperatures. At higher temperatures the products are CrF_5 and CrF_4. It therefore appears that replacement of the third oxygen atom initially gives chromium hexafluoride; this decomposes to the pentafluoride, which is itself subject to decomposition to the tetrafluoride at elevated temperatures.[11]

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Chromium oxide tetrafluoride reacts with Pyrex glass apparatus. After several weeks at room temperature, $CrOF_4$ in sealed ampoules formed CrO_2F_2. The presence of the dioxide difluoride was verified by *X*-ray examination of single crystals.[12] After a further period, a bright red, involatile solid was formed, which was shown to be chromium trioxide by *X*-ray powder photography.

TABLE 1

Mass spectrometric cracking patterns of CrO_2F_2, $CrOF_4$, CrF_5, and CrF_4

	CrO_2F_2				$CrOF_4$				CrF_5			CrF_4		
Source temp (°C)	25						86	25	25			101		
Orifice size (cm)	0·02						0·02	0·02	0·02			0·02		
			Relative intensity				Relative intensity							
	m/e	Ion	This work	Ref. 9	*m/e*	Ion			*m/e*	Ion	Relative intensity	*m/e*	Ion	Relative intensity
	122	$CrO_2F_2^+$	58	58	144	$CrOF_4^+$			147	CrF_5^+	5	128	CrF_4^+	43
	106	$CrOF_2^+$	47	42	125	$CrOF_3^+$	100	100	128	CrF_4^+	100	109	CrF_3^+	100
	103	CrO_2F^+	23	22	109	CrF_3^+	17	7	109	CrF_3^+	85	90	CrF_2^+	18
	90	CrF_2^+	100	100	106	$CrOF_2^+$	45	43	90	CrF_2^+	25	71	CrF^+	17
	87	$CrOF^+$	23	16	90	CrF_2^+	26	22	71	CrF^+	32	52	Cr^+	28
	71	CrF^+	20	11	87	$CrOF^+$	12	12	52	Cr^+	38			
	68	CrO^+	6	3	71	CrF^+	20	19						
	52	Cr^+	23	16	68	CrO^+	2	2						
					52	Cr^+	25	21						

Relative intensities are reported for the ^{52}Cr isotope; 70 eV electron energies.

The vapour pressure data for $CrOF_4$ are summarised by the following equations:

Solid $CrOF_4$ (below 24·1°) $\log p$ (Torr) =
$$13{\cdot}22 - 3546/T$$

Solid $CrOF_4$ (24·1 – 55·2°) $\log p$ (Torr) =
$$10{\cdot}48 - 2732/T$$

Liquid $CrOF_4$ (55·2 – 70°) $\log p$ (Torr) =
$$8{\cdot}78 - 2174/T$$

The value of the triple point determined by the solution of the equations was 55·2°, and was in good agreement with the m.p. determined directly in a thin-walled capillary. The solid–solid transition point of 24·1° was obtained from the intersection of the two sublimation curves.

The b.p. found by extrapolation is 95°. This could not be checked directly owing to rapid attack of Pyrex glass apparatus at temperatures above 70°. Thermodynamic values were derived from the vapour-pressure data using the Clapeyron–Clausius equation. The heats of sublimation are 67·7 kJ mol^{-1} for the solid below 24·1 °C and 52·4 kJ mol^{-1} above this temperature, and the heat of transition is 15·5 kJ mol^{-1}. The heat of vaporisation is 41·6 kJ mol^{-1}, the heat of fusion 10·7 kJ mol^{-1}, and the entropy of vaporisation 113 J mol^{-1} K^{-1}.

The vapour pressure measurements show that the physical properties of chromium oxide tetrafluoride are unlike those of the oxide tetrafluorides of second- and third-row transition elements.[13] The much smaller liquid range is the most noticeable difference, and a similar difference is found in a comparison of vanadium pentafluoride with the second- and third-row transition metal pentafluorides (Table 2).

The solid–solid transition found for $CrOF_4$ is paralleled only by $TcOF_4$ of the other oxide tetrafluorides.[5,14] The low-temperature form of $CrOF_4$ (below 24·1°) has an endless chain structure, similar to that of $MoOF_4$ and $ReOF_4$, although the details of this structure have not been fully elucidated.[14] The transition may therefore correspond to a rearrangement of the packing of these chains in the crystal, although no *X*-ray measurements have yet been made on the high-temperature form.

TABLE 2

Comparison of physical properties of some transition metal pentafluorides and oxide tetrafluorides

Compound	M.p.(°C)	B.p.(°C)	Compound	M.p.(°C)	B.p.(°C)
$CrOF_4$	55	95	VF_5	19	48
$MoOF_4$	97	186	NbF_5	80	235
$RuOF_4$	115	184	MoF_5	67	214
WOF_4	105	186	RuF_5	86	227
$ReOF_4$	108	172	ReF_5	48	221

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