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Low-temperature Cr(III)OCl: X-ray powder diffraction patterns

R. E. SOWDEN

(Abstract)

The crystal structure of high-temperature Cr (III) OCl is known but nevertheless there exist no previously published X-ray diffraction data suitable for routine identification purposes.

In the present work Cr (III) OCl was prepared free from crystalline Cr_20_3 at the relatively low temperature of 590°C by reacting dried chromic hydrate with anhydrous $CrCI_3$.

Low-temperature samples of Cr (III) OCl prepared using low-temperature and high temperature $CrCl_3$ were examined with a Guinier camera. The X-ray powder diffraction pattern of the former sample of Cr (III) OCl was also indexed in the range $2\theta = 10 - 63°$ with a diffractometer. The three strongest lines observed were 7.67 dA (100 I/I_o), 3.441 (100) and 2.441 (60).

The X-ray powder diffraction data obtained, along with previously unpublished reference data for high-teperature Cr (III) OCl, are tabulated in a form suitable for routine identification purposes.

Pure chromium oxychloride, Cr (III) OC*l*, is usually prepared [1] by means of the vapour transport reaction occurring at temperatures in the range 715–1060°C between (i) anhydrous $CrCl_3$ and either H_20 or an anhydrous metal oxide such as Bi_20_3, TiO_2, SiO_2or Cr_2O_3, or (ii) $SiCl_4$ and Cr_2O_3. No low temperature method is recorded in the literature. Furthermore, although the crystalline structure of CrOCl has been elucidated with some certainty with X-ray diffraction techniques [1 – 2] – it consists of layers of –Cr–0–Cr–0–separated by double sheets of chlorine with the following bond lengths:

Cr – O	0.197 – 0.201 nm
Cr – Cl	0.232 nm
Cr – Cr	0.304 nm

and with no metal-metal interaction – there exist no published XRD data on CrOCl in a form suitable for routine identification purposes.

In the course of investigating the low-temperature chloridisation of chromic oxide, Cr (III) OCl was prepared at the relatively low temperature of 590°C and X-ray powder diffraction patterns obtained.

MATERIALS

Chromic hydrate, $Cr_2O_3.xH_2O$, and anhydrous $CrCl_3$ were prepared using 'AnalaR' grade reagents supplied by Hopkin and Williams Ltd. [3].

$Cr_2O_3.xH_2O$: 0.23 l of a gently agitated 0. 29 M solution of $CrCl_3.6H_2O$ was neutralised with 35 % ammonia solution. The precipitated chromic hydrate was filtered, washed thoroughly with distilled water and dried in air for 3h at 110°C. It contained 34.2 % Cr, 0.00 % Cl, and was amorphous to X-rays; loss on ignition was 46.6 % at about 700°C.

Low-temperature $CrCl_3$: $CrCl_3$ was prepared at a low temperature by chloridising lg of the dried and ground ammonia-precipitated chromic hydrate with carbon tetrachloride vapour, using oxygen-free nitrogen as carrier gas, for 4h at 430°C (space velocity of carrier gas: 156 mm min^{-1} at S.T.P.; partial pressure of CCl_4: 85 mm Hg) [4] in a silica boat in a horizontal tubular furnace. The low-temperature $CrCl_3$ product contained chloride and chromium in molar ratio 3.00: 1, was non-hygroscopic, and exhibited X-ray powder diffraction patterns, infra-red absorption spectrum (range: 1-21 nm) and diffuse reflectance spectrum (range: 400-700 nm) similar to those of a reference sample* of sublimed, high-temperature $CrCl_3$ (33.3 % Cl, 66. 0 % Cr) prepared by the usual method of direct chlorination of crystalline, anhydrous Cr_2O_3 followed by sublimation in a stream of dry chlorine gas.

EXPERIMENTAL

Samples of the chromic hydrate and $CrCl_3$ werefinely ground, weighed, intimately mixed, placed in a silica boat and heated in the horizontal tubular furnace in an inert atmosphere as follows:

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* Prepared by R. L. Foreman, Department of Metallurgy, Royal School of Mines

Sample A: 0.165g of the chromic hydrate, previously heated for 1h at 430°C in an atmosphere of nitrogen, was heated with 0.127 g of the low-temperature $CrCl_3$ for 1h at 590°C in a stream of nitrogen gas (space velocity: 156 mm min^{-1} at S.T.P.).

Sample B: 0.422 g of the dried and ground but otherwise untreated chromic hydrate was heated with 0.235g of the high-temperature $CrCl_3$ for 0.5h in a stream of nitrogen gas of nitrogen gas (space velocity: 156 mm min^{-1} at S.T.P.).

After reaction, samples A and B were cooled in a stream of nitrogen and re-weighed. They were then ground, mounted without internal standard between strips of Sellotape, and placed in a Guinier camera using Cu-Kx radiation. The X-ray powder diffraction patterns obtained were examined with a simple diffraction spacing rule; a Sellotape blank was used

The X-ray pattern given by sample A was indexed in the range $2\theta = 10 - 63°$ using a General Electric Diffractometer Model XRD6 without internal standard.

RESULTS AND DISCUSSION

X-ray powder diffraction patterns obtained with Samples A and B, screened for Sellotape, are presented in Table 1: the Sellotape blank gave the weak pattern 4.45 dA (I/I_0 100), 4.05 (100), 3.02 (10). Cr(III) OCl was identified as the only crystalline compound present in the two samples in significant amounts by comparing the above X-ray patterns with the previously unpublished reference data [5] for CrOCl given in Table 1.

The absence of the diffraction pattern of $CrCl_3$ [6], 2.460dA (I/I_0 100), 5.80 (80), 1.718 (80), in the samples suggests that the reaction forming CrOCl was fairly fast and efficient, for $CrCl_3$ is negligibly volatile [7] in the conditions employed in the present work. Samples A and B contained 125 % and 100 % respectively of the theoretically stoichiometric amount of chromic hydrate according to the supposed stoichiometric equation:

$Cr_2O_3 . xH\,O$ (amorph.) $+ (1+x)CrCl_3(c) = (3+x)\,CrOCl(c) + 2xHCl\,(g)$

Table 1. XRD Patterns of Cr (III) OCl

Sample				Reference data (5)	
A		B		CroCI	
dA	I/I_o	dA	I/I_o	dA	I/I_o
7.67	100	7.7	100	7.55	m
		5.46	1		
4.34	5				
3.61	10	3.61	30		
3.441	100	3.43	70	3.45	ms
2.648	5	2.64	40		
2.465	20	2.46	50		
2.441	60	2.44	80	2.450	ms
2.326	20	2.32	1	2.340	mw
2.17	1	2.16	1	1	
				2.062	vw
1.991	2			1.994	mw
1.924	30	1.981	2	1.922	m
1.864	1			1.870	w
1.767	2	1.76	1	1.774	m
				1.728	vw
		1.702	20		
1.668	3	1.658	10		
1.590	1			1.586	w
1.584	1	1.576	1		
1.512	5	1.508	1	1.516	m
1.459	1	1.457	1		
1.438	1				
		1.422	1		
		1.420	1		
				0.8337	w

Abbreviations: s-strong; w-weak; m-medium; v-very

derived by analogy with equations previously proposed [1] for the transport reactions occurring between crystalline chromic oxide and chromic chloride in the temperature range 840 – 1040°C:

$$Cr_2O_3(c) + CrCl_3(c) = 3\,CrOCl(c)\ (\Delta G^\circ, 1300K: -38kJ\ mol^{-1})$$

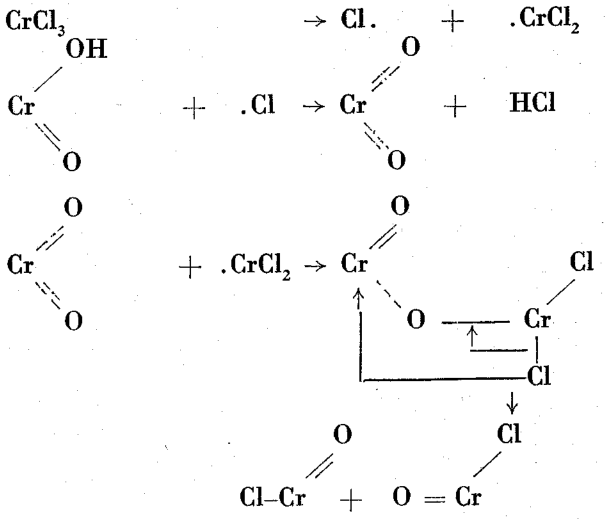
and between water vapour and chromic chloride in the temperature range 750 – 1000°C:

$$CrCl_3\ (3) + H_2O(g) = CrOCl\ (c) + 2HCl\ (g)\ (\Delta G^\circ,\ 1000K: -92kJ\ mol^{-1})$$

The experimental loss in weight of samples A and B upon reaction was found to be 10.0 % and 33.0 % respectively, which compares favourably with the theoretically calculated values, 8 % and 31 %.

The absence of the XRD pattern of Cr_2O_3. 10R [8], 2.666dA ($I/I_0$100), 2.480 (95), 1.672 (90), 3.633 (75), in the products indicates that any residual chromic oxide remained in the amorphous state. This is significant because it was found in simultaneous TG-DTA studies that the chromic hydrate exhibited a twin-glow exotherm in nitrogen with peaks at 590 °C and 630 °C (chromic hydrate vigorously recrystallises with simultaneous loss of the last traces of moisture when heated to the 'glow' temperature [9]). It would seem therefore that the reaction forming CrOCl does not arise directly from the glow phenomenon. This was confirmed by reacting magnesia-precipitated chromic hydrate (exhibiting a single, attenuated glow peak in nitrogen at 715 °C) with $CrCl_3$. CrOCl was formed at 590 °C and no crystalline Cr_2O_3 was observed in the product.

When a sample of chromic hydrate that had previously been dehydrated for 1h at 590 °C in an atmosphere of nitrogen was similarly heated with $CrCl_3$ at 590 °C in a stream of nitrogen gas neither CrOCl nor crystalline Cr_2O_3 was detected in the product. Apparently chromic hydrate and $CrCl_3$ react to form CrOCl in an inert atmosphere at 590 °C only if the chromic hydrate is sufficiently hydrated. A possible reaction mechanism is described below:



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ÖZET

Yüksek-sıcaklık Cr (III) OCl'nin kristal yapısı biliumekle beraber, rutin teşhisler için yayınlanmış bir X-ışını kırınım verileri bulunmamaktadır.

Bu çalışmada kristalin Cr_2O_3 ten kurtarılmış Cr (III) OCl oldukça düşük sıcaklıkta (590°C) kurutulmuş krom hidrür susuz $CrCI_3$ ile etkileştirilerek hazırlanmıştır.

Önceki Cr (III) OCl örneğinin X-ışını kırınım deseni $2\theta = 10-63°$ aralığında bir difraktometre ile ayrıca indekslendi. Gözlenen üç en kuvvetli çizgi 7.67 dA (I/I_o 100), 3.441 (100) ve 2.441 (60) idi.

Daha önce yüksek sıcaklık Cr (III) OCl için yayınlanmamış fererans verileri yanıuda, elde edilen X-ışını kırınım verileri, rutin tanımlamp (teşhis) amaçlarına uygun şekilde düzenlenmiştir.

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