[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Products of Thermal Decomposition of Chromium Trioxide[1,2]

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The products of the thermal decomposition of chromium trioxide have been studied by means of X-ray diffraction and chemical analysis. Three compounds intermediate between CrO_3 and Cr_2O_3 have been found. These are Cr_3O_8, Cr_2O_5 and CrO_2. By using oxygen pressures up to 900 p.s.i. in the temperature range 322 to 563°, the preparation of each of these oxides in relatively pure form was accomplished. No evidence was obtained for the existence of oxide phases of variable composition. It appears likely that some of the formulas previously ascribed to oxides of chromium are derived from the analysis of heterogeneous mixtures.

The black products which are obtained as intermediates in the thermal decomposition of chromium trioxide to chromic oxide have been studied by many investigators but there is considerable disparity among their conclusions.

From weight changes observed in heating chromium trioxide *in vacuo* Simon and Schmidt[4] found that Cr_5O_{13} was formed between 260 and 280° and Cr_5O_{12} between 360 and 366° and these were the only intermediate oxides. From pressure measurements, on the other hand, Ryss and Selyanskaya[5] came to the conclusion that the oxides Cr_5O_{13}, Cr_8O_{21}, Cr_7O_{18} and Cr_5O_{12} were formed. A different idea was presented by Cameron, Harbard and King[6] who studied the volume of oxygen liberated from chromium trioxide at constant pressure as a function of temperature. The volume–temperature curves showed gradual changes at approximately 250 and 360° extending over composition ranges $CrO_{2.6-2.2}$ and $CrO_{1.9-1.7}$ which they interpret as an indication of non-stoichiometric compound formation. More recently, Vasenin[7] from differential thermal analysis reported that only Cr_2O_5 is formed between 267 and 348°. He gave the X-ray diffraction powder pattern of the product. Changes in magnetic susceptibility of chromium trioxide and its products during thermal decomposition suggested to Honda[8] that two compounds Cr_6O_{15} and Cr_5O_{19} were formed successively. The latter is ferromagnetic and was obtained at 450°. A subsequent publication by Michel and Benard[9] establishes the ferromagnetic oxide as CrO_2 which has the rutile structure.

This paper gives the results of the examination of decomposition products of chromium trioxide by X-ray diffraction and chemical analysis.

The thermal decomposition was carried out first in an evacuated apparatus and later under relatively high oxygen pressures.

Experimental

A sample of about 5 to 10 g. of dried, reagent grade chromium trioxide in a silica glass boat was placed in an assembly of two Pyrex test-tubes, the mouth of the smaller tube being toward the closed end of the larger. This served to prevent sublimation of the chromium trioxide to the cooler parts of the reaction tube. The reaction tube was placed in the cold furnace, the system evacuated and the furnace allowed to reach the desired temperature which was held to ±2°. The heating was continued until constant pressure was reached. The temperature range was 210 to 460° and the heating periods varied from 20 to 200 hr.

X-Ray diffraction patterns were obtained for all the products. By visual comparison of these patterns, the presence of several phases could be detected by the appearance and disappearance of certain sets of diffraction lines from one pattern to another. In this way it was possible to arrive at the powder patterns for three different phases which are listed in Table I. These are numbered in order of their formation with rising temperature. None of the products consisted of a single phase.

TABLE I

X-RAY POWDER PATTERNS

Phase I (Cr_3O_8)		Phase II (Cr_2O_5)		Phase III (CrO_2)	
d (Å.)	Intensity	*d* (Å.)	Intensity	*d* (Å.)	Intensity
11.8	M				
6.19	W	8.45	MS	3.13	S
5.84	W	6.24	M	2.435	M
4.95	VVW	5.95	M	2.213	VW
4.49	VW	5.13	VVW	2.135	W
3.88	S	3.87	VW	1.638	MS
3.72	M	3.48	W	1.566	W
3.34	MS	3.26	S	1.459	VW
3.21	W	3.08	VVW	1.382	VW
3.08	MS	3.81	W	1.318	W
2.95	VW	2.75	VW	1.066	VW
2.81	VVW			1.016	VVW
2.67	VW			0.850	VVW
2.60	VW			0.812	VW
2.13	VVW			0.793	VVW
2.014	VVW				
1.938	VVW				
1.856	VVW				
1.718	VVW				
1.659	VVW				
1.511	VVW				
1.351	VVW				

Below 360° the products were principally mixtures of I and II with small amounts of III. Extraction of this mixture with water gave a residue which was essentially phase II contaminated with phase III. Between 360 and 460° the main ingredient of the product was chromic oxide with small amounts of phase III.

Since it appeared likely that a stepwise decomposition was occurring, the reaction was carried out under high oxygen pressure in the hope that conditions could be adjusted to yield each of the phases in relatively pure form. This was accomplished by means of a steel bomb consisting of a thick-walled steel cylinder to the open end of which a machined cover was bolted. An annealed copper gasket was used between the cylinder and cover. The cylinder was attached to a commercial oxygen cylinder by means of S.A.E. flare

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(4) Simon and Schmidt, *Z. anorg. Chem.*, **153**, 191 (1926).

(5) I. G. Ryss and A. I. Selyanskaya, *Acta Physiochem.* (*U. S. S. R.*), **8**, 623 (1938).

(6) A. Cameron, E. H. Harbard and A. King, *J. Chem. Soc.*, 55 (1939).

(7) F. I. Vasenin, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 459 (1947).

(8) Honda, *Sci. Rep. Tohoku Univ.*, **3**, 223 (1913).

(9) A. Michel and J. Benard, *Compt. rend.*, **200**, 1316 (1935).

fittings and copper tubing. A metal Bourdon gage was used to determine the pressure.

A weighed quantity of dried chromium trioxide in a Pyrex tube with a loosely fitting cover was placed in the bomb which was then flushed with oxygen several times and charged with oxygen to the desired pressure. The bomb was then placed in a vertical tube furnace and brought to temperature, the pressure being maintained constant by a manually operated valve. The reaction was stopped by quenching the bomb in ice-water. The conditions and results of a number of experiments are given in Table II.

TABLE II

PRODUCTS OF THERMAL DECOMPOSITION OF CrO_3 UNDER OXYGEN PRESSURE

Temp., °C.	Pressure, p.s.i.	Time, min.	Phases
322	50	120	I[a]
322	300	120	I[a]
441	25	60	II + trace III
441	50	210	II + III + Cr_2O_3
441	300	90	II + trace III
441	500	120	II + trace III
495	300	120	II + trace III
513	300	5	II + III
545	200	10	II[a]
545	900	60	Trace II + III
545	900	75	II + III
545	900	90	Trace II + III
545	900	120	III + trace Cr_2O_3
563	300	180	III + Cr_2O_3

[a] Samples used for analysis.

These data show that the decomposition of phase I can be arrested at 322° with moderate oxygen pressures so that none of the strongest lines of phase II or III appear in the diffraction patterns. Phase II is the main product in the temperature range 441 to 495 at oxygen pressures above 300 p.s.i. and with heating periods up to 2 hours. It is usually contaminated with phase III under these conditions. The purest samples of phase II were obtained at 545° under 200 p.s.i. for 10 minutes. Longer heating periods at 545° with the oxygen pressure at 900 p.s.i. usually gave phase III as the principal product but none of these samples was sufficiently pure to warrant the establishment of the formula by chemical analysis.

The samples indicated in Table II were used for analysis of phases I and II. Phase I was readily soluble in water giving a solution containing both CrO_4^{-2} and Cr^{+3}. The chromate was determined in an aliquot by titration with standard ferrous sulfate solution using barium diphenylamine as indicator. Another aliquot was treated with hot 70% perchloric acid to oxidize the Cr^{+3} to CrO_4^{-2} and the total chromium determined by titration. The average oxidation number of chromium was thus found to be 5.34 and the percentage chromium 55.2. This corresponds to the formula Cr_3O_8 (54.93% Cr).

A weighed sample of phase II was dissolved in boiling 70% perchloric acid and the total chromium determined to be 56.8 which corresponds reasonably well to Cr_2O_5 (56.5% Cr). Perhaps it is of interest to note that the X-ray diffraction pattern used by Vasenin to substantiate the formation of Cr_2O_5 as an intermediate in the decomposition of chromium trioxide corresponds to that of a mixture of Cr_3O_8, Cr_2O_5 and Cr_2O_3.

Phase III corresponds to the rutile type oxide and presumably has the ideal formula CrO_2.

The ranges of variable composition in the oxides $CrO_{2.2-2.6}$ and $CrO_{1.7-1.9}$ reported by Cameron, Harbard and King[6] should lead to some detectable variation in lattice spacings. This could not be checked very well for Cr_3O_8 and Cr_2O_5 since the diffraction patterns of the compounds we obtained did not have any back-reflection lines. No variation in the spacings was detectable with the forward reflection lines. In the case of chromium dioxide, on the other hand, the lines in the back reflection region were quite adequate. Two samples were carefully examined; one which was contaminated with Cr_2O_5 and another which contained Cr_2O_3. These samples represent the oxide intermixed with phases of higher and lower oxygen contents. The cell dimensions in these cases should represent the extremes in composition of the oxide. Examination of the lines that correspond to Bragg angles close to 78° show that the lattice constants cannot have differed over the extremes of composition by more than 2 parts in a thousand. This indicates that marked non-stoichiometry is not possible and that the range of non-stoichiometry is rather limited. This interpretation is consistent with the fact that the relative intensities of the lines in the diffraction pattern did not change in any case.

Formulas such as Cr_8O_{21}, Cr_5O_{13}, Cr_7O_{18}, Cr_5O_{12}[5] and Cr_5O_9[8] were arrived at by interpretation of pressure measurements and magnetic susceptibility data neither of which is unequivocal. It is most likely that the products analyzed were all heterogeneous. While it must be admitted that our analytical data are not sufficiently precise to distinguish between Cr_2O_5 and Cr_7O_{18} or between Cr_3O_8 and Cr_8O_{21}, we are inclined to favor the simpler formulas until the necessity for a more complex one can be demonstrated. The complete determination of the crystal structure of these two phases could settle this point.

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