REACTIONS OF CHROMATES AT HIGH TEMPERATURES.

PART IX. THERMAL DECOMPOSITION OF CHROMIUM TRIOXIDE.

By

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INTRODUCTION.

In Parts III to VIII of this series (This Journal, **20A**, 55–56, **21A**, 109–129, 159–169, 179–188, 273–283 and **22A**, 111–118) it was shown that the decomposition of calcium, strontium and barium chromates, proceeded through four stages corresponding to 50, 66.6, 75 and 80 % of the complete decomposition. The higher stages of decomposition could not be obtained in the case of barium chromate. The decompositions of the mixtures of the chromates with the corresponding oxides indicated stages at 25, 33.3 and 40 %. The various stages were identified by their characteristic decomposition pressures. It was therefore interesting to find out whether chromium trioxide CrO_3 showed a similar stepwise decomposition.

HISTORICAL.

The existence of various chromium chromates or the oxides intermediate between CrO_3 and Cr_2O_3 including CrO_2, Cr_3O_5, Cr_8O_{21}, Cr_5O_9, Cr_6O_{15}, Cr_4O_9, Cr_5O_{13}, Cr_7O_{15}, Cr_5O_{12} and Cr_8O_{15}, has been previously reported in literature. These oxides have been obtained by different chemical methods, and by the thermal decomposition of CrO_3, and their properties have been studied extensively [*cf.* recent references on the subject: Blanc, (Ann. Chim. Phys. 1926, (10) **6**, 182); Blanc and Ghaudren (Comptes. rend. 1926, 186, 386), Jovitschi'sch (Helve. Chim. Acta, 1920, **3**, 40), Ridley (Chem. News, 1924, 129, 35), Hayes (Amer. J. Science, 1928, **14**, 136; 1931, **20**, 409) and Calcagni (Gazz. chim. Ital., 1925, **55**, 226)].

The earliest attempt to study the thermal decomposition of CrO_3, appears to have been made by Dobereiner (Schweigger's Jour. 1818, **22**, 476) and M. Traube (Liebigs Ann. 1848 **66**, 87). They state that Cr_5O_{12} or normal chromium chromate is formed when chromic anhydride is heated to about 250°. Schukoff (Jour. Russ. Phys. Chem. Soc. 1909, **41**, 302 and Comptes rend. 1908, **146**, 1396) obtained Cr_4O_9 by heating chromic anhydride to 500°—510° and found that the magnetic properties of this oxide disappeared at 120°—130° and reappeared on cooling. Honda (Science rep. Tohoku Univ. 1915, **4**, 97) observed that when chromic acid is heated there is just an expulsion of moisture with the formation of Cr_6O_{15} at 300° and of Cr_5O_9 at 420°, the decomposition being complete at 450°. These results were in accordance with the observations of Honda and Sone (Ibid. 1914, **3**, 223), who found that Cr_6O_{15} is formed at about 280° and Cr_2O_3 at 420°, and that the strongly paramagnetic Cr_6O_{15} and the ferromagnetic Cr_5O_9 are present as mixtures at the intermediate temperatures. Simon and Schmidt (Zeit. Anorg. Chem. 1926, 153, 191) could not obtain the two above mentioned oxides. They reported the existence of the two other intermediate oxides, viz., Cr_5O_{13} and Cr_5O_{12}. Nargund and Watson, (*This Journal*, 1926, **9**, 149) studied the decomposition of chromic acid at atmospheric pressure and obtained an indication of a stage at 50 %, corresponding to the formation of a compound Cr_4O_9. Ryss and Seljanskaja (Acta Physica Chemica 1938, **5**, 623–40) obtained the two oxides Cr_5O_{13} and Cr_5O_{12} in confirmation of the observations of Simon and Schmidt. The product obtained by heating chromic anhydride between 241° – 300° were mixtures of 24.9 and 28.5 % stages and various formulae Cr_8O_{21}, Cr_7O_{18} Cr_5O_{13} were assigned to the compound formed. The oxide Cr_5O_{12} was obtained by decomposition at 360°, which on further heating at 400° completely decomposed to Cr_2O_3. Addition of quartz and iron powder accelerated the decompositions and yielded two more stages corresponding to the formation of Cr_6O_{15} and Cr_5O_9.

It appears from the survey of the literature (*cf.* Mellor, Comprehensive Treatise on Inorganic and Theoritical Chemistry 1931, 206-211), that the individuality of these oxides has not yet been well established and the evidence for the formation of CrO_2 and Cr_8O_{15} in the thermal decomposition of CrO_3 is lacking, and data for the other intermediate oxides is insufficient and not conclusive.

EXPERIMENTAL.

The apparatus used and method of experimentation have already been described in the previous parts of this series. The chromic acid (fused) supplied by 'E de Haen' was used for the study of the decomposition.

The decomposition of CrO_3 was determined from the loss of oxygen in the reaction according to the following equation :

$$2CrO_3 = Cr_2O_3 + \tfrac{3}{2}O_2.$$

Honda calculated the decomposition by measurement of the loss of weight of the substance, and Ryss and Seljanskaja, by the pressure measurements. We measured the volume of oxygen evolved after pumping out the gas from the apparatus by Topler pump whenever necessary. The pressure measurements were found useful in determining the composition of the oxides at various stages, from a knowledge of the volume of the apparatus.

The stability of the decomposition products at different temperatures served as a useful criterion for identifying the intermediate oxides. Honda utilized the magnetic measurements of the different oxides as an additional evidence for the formation of different oxides in the decomposition of CrO_3, which will be discussed in next Part.

It was observed that different oxides decomposed with a uniformly constant rate when the temperature was kept constant, thus showing that the rate of decomposition was a distinctive property of the compound and depended on temperature. We have availed of this property for distinguishing the formation of different stages.

Decomposition of CrO_3 :

The melting point of CrO_3 is near about 185°, at which decomposition starts, in confirmation of the observation of Ryss and Seljanskaja. The decomposition reaction is irreversible and attempts to measure the equilibrium pressures at different temperatures failed.

There is no equilibrium between CrO_3 and the next stage. The rate of decomposition was however constant and independent of the concentration of the reacting molecules in the various phases. The reaction thus does not obey the law of unimolecular reaction as was supposed by Ryss and Seljanskaja but is of the zero order. We have calculated the velocity constant of the reaction by the amount of oxygen evolved. The logarithm of the velocity constants when plotted against the reciprocal of the absolute temperatures yielded a straight line for the different stages (Fig. 1). The heat of activation for each oxide was then calculated by the application of the Arrhenius equation.

Table I shows the rates of decomposition in terms of increase

TABLE I.
Weight of CrO_3 taken = 2.9546 gms.

	Stage % decomposed	Oxide	Temp. °C	Rate mm./hr.	Heat of activation Cals.	Stability Temp. °C
A		CrO_3	245 247 253	17.0 18.0 22.0	16.9	185
B	25 %	Cr_8O_{21}	286 304 321	3.2 8.0 28.5	41.4	250
C	33.3 %	Cr_6O_{15}	295.5 318 346 361	0.6 4.3 17.0 50.0	47.2	290
D	40 %	Cr_5O_{12}	372 378 398	26.0 33.0 55.0	26.5	349
E	50 %	Cr_4O_9	288 320 323 357 363	0.24 1.08 2.1 14.4 2.8	41.5	287

in pressure in mm. per hour for different oxides at different temperatures, the heat of activation for different oxides and the range of stability as given by the temperature above which each of the oxides begins to decompose.

The decomposition rates of CrO_3 to the 25% stage have been shown in Fig. (1).

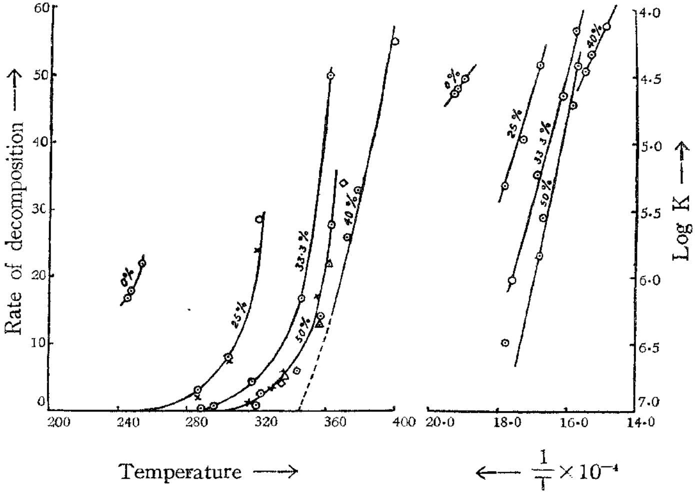

Fig. (1)

⊙—⊙ Rate of decomposition of the chromium chromates.
×—× ,, ,, after 29% and 66.6%
△—△ ,, ,, ,, 75%
□—□ ,, ,, ,, 80%

25% decomposition stage, Cr_8O_{21} :

After a prolonged heating of CrO_3 at 250°, the rate of decomposition of CrO_3 dropped from 22 mm. to 0 mm. when the decomposition reached 25.5%. There is thus a clear indication of the formation of a new stage. The formula of the compound corresponding to 25% decomposition is Cr_8O_{21}. We have measured the rate of decomposition of this compound at different temperatures. The results are shown graphically and tabulated, in Fig. 1 and Table 1 B.

As already mentioned, Ryss and Seljanskaja (loc. cit) obtained oxides varying in composition between 24.9 and 28.5%, and the mean value indicated the formation of Cr_5O_{13} (26.86%), which was also found by Simon and Schmidt. They obtained the heat of activation of the compound as 33.97 cals. (applying the law of unimolecular reactions). The possibilty of the partial decomposition of the 25% compound to the 33.3% stage, appears to have been ignored. It is very essential to keep the system for at least two days to allow reactions between the solids to proceed at such comparatively low temperatures.

It was observed that the rate of decomposition at different temperatures was the same until the next stage, viz., 33.3% stage was formed. There was no indication of the formation of the 28.86% decomposition stage in our work.

33.3 % decomposition stage, Cr_6O_{15} :

25% compound was further decomposed at 286° and a drop in the rate of decomposition from 3.2 mm. to 0 mm. was observed, when the decomposition was 34%. The compound formed was found to be stable up to 290°. The rates of further decomposition at different temperatures are given in Table I (C) and shown in Fig. I.

40 % decomposition stage, Cr_5O_{12} :

The decomposition was studied at 346° and the rate of decomposition measured by the pressure increase per hour, dropped from 17 mm. to 0 mm., when the composition of the solid phase indicated 40 % decomposition. The decomposition of the latter appears to begin at 349°. The values for the rate of decomposition for this oxide were determined, and the heat of activation calculated in the usual way.

50% decomposition stage, Cr_4O_9:

The 40 % compound was further decomposed at 357°. There was no change in the rate of decomposition until the composition of the solid stage corresponded to Cr_4O_9, or the 50% stage. At this temperature there seems to be a marked difference between the rate of decomposition of the 40% stage and of the 50 % stage, the decomposition rate of the latter being slightly more. As this stage was previously obtained by Nargund and Watson by heating the oxide in air, the reaction was arrested by lowering the temperature, and the range of stability was studied. The compound was less stable than 40 % and possessed distinctively different rates of decomposition at different temperatures, as can be seen from the results given in Table I E and Fig. 1.

66.6 %, 75 % and 80 % stages:

There is practically no evidence for the formation of these stages in the decomposition of CrO_3 by heating. It was observed that when the decomposition reached 66.6, 75 and 80%, the rates of decomposition were the same as that for 50 % stage. From the results shown in Fig. (1) it would appear that the compound formed at 50 % stage decomposes directly to Cr_2O_3 without formation of any intermediate oxide, because the rate of decomposition at different temperatures at various stages when the composition of the solid phase was intermediate between 50 % and 80 %, is the same as that of the product formed at 50 % decomposition.

Simon and Schmidt (loc. cit) while studying the decomposition of hydrated CrO_2 (66.6 % decomposition) and Cr_8O_{15} (75 % decomposition) observed that the compounds are stable only as hydrates and that both water vapour and oxygen are evolved side by side on heating these oxides.

Ryss and Seljanskaja have obtained the 80 % stage in the decomposition of CrO_3 in presence of cast iron. As iron is oxidised in the process, it is probable that iron chromium chromates are formed, which are probably more stable.

SUMMARY.

The thermal decomposition of chromium trioxide has been studied in a closed system maintained at constant temperature by following the rate of decomposition at various stages. The results indicated the formation of intermediate compounds at 25%, 33.3%, 40% and 50% of the complete decomposition which were characterised by distinctive rates of decomposition, and heats of activation.

The existence of the above stages in the decomposition of the chromium trioxide is in agreement with the previous results obtained in the decompositions of the mixtures of chromates of the alkaline earths with the corresponding oxides.

There was apparently no stage at 26.86%, which was obtained by previous workers. The higher stages at 66%, 75% and 80%, obtained in the decomposition of the pure chromates reported previously, if they exist, are not characterised by appreciably different rates of decomposition.

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