178. *The Thermal Decomposition of Ammonium Dichromate.*

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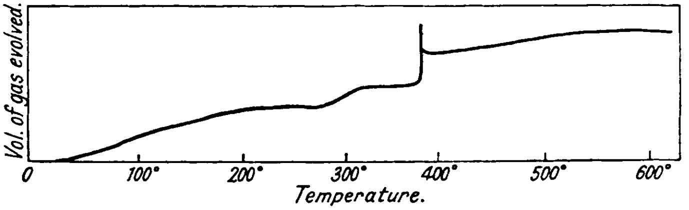
On ignition of ammonium dichromate in a vacuum or at atmospheric pressure, at a temperature below its normal point of decomposition, a black product is obtained which has been variously identified as hydrated chromic oxide or chromium dioxide, but as it has now been shown that nitrogen and nitrous oxide are evolved in its decomposition, it is probably a solid solution of two or more compounds.

On ignition of the above material or on the direct thermal eruption of ammonium dichromate, an olive-green voluminous powder is obtained which is usually assumed to be chromic oxide. As a result of numerous analyses it is now established that this compound contains more oxygen than does chromic oxide, and that the excess oxygen is not easily lost on reduction with hydrogen. This compound is probably a non-stoicheiometric oxide of chromium.

ALTHOUGH the decomposition of ammonium dichromate is still usually represented as $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4H_2O$, previous workers have noticed that ammonia and oxides of nitrogen are present in appreciable quantities amongst the products.

By heating ammonium dichromate for a considerable time just below the temperature at which it normally decomposes violently, Ball (J., 1909, **95**, 87) obtained a homogeneous black powder which he identified as hydrated chromium dioxide, $3CrO_2,H_2O$; considerable quantities of ammonia and oxides of nitrogen were evolved in this reaction. Hooton (*Proc. Roy. Soc.*, 1908, **24**, 27) obtained a black product under similar conditions but formulated it as $H_2Cr_2O_4$; heated in oxygen, it formed $2CrO_2,H_2O$. Moles and Gonzalez (*Anal. Fís. Quim.*, 1923, **21**, 204), using a similar method of preparation, obtained a black crystalline compound which they identified as CrO_2 by ignition to chromic oxide. Fischbeck and Spingler (*Z. anorg. Chem.*, 1938, **235**, 185) have now described the preparation of a black compound by decomposing ammonium dichromate at a pressure of about 10^{-4} mm. and indicate that it has the composition Cr_2O_3,H_2O, the decomposition being represented as $(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3,H_2O + 3H_2O$. Apparently, most of these earlier workers analysed their compounds by ignition to an end product presumed to be chromic oxide; but (see p. 957) this assumption is hardly permissible.

As a prelude to the study of the surface properties of the oxides of chromium, we carried out the decomposition of ammonium dichromate in a vacuum and obtained a light, black, hygroscopic powder which appeared under the microscope to be highly porous but homogeneous; it was insoluble in all acids and in aqueous solutions of alkalis. In view of the disagreement as to the composition of this material we investigated it. The washed and dried powder was quantitatively analysed for chromium by alkaline fusion and conversion into dichromate. A weighed quantity of the material was then decomposed by heating it in a closed tube, the gas evolved being collected in a gas burette. The system was allowed to reach equilibrium before each increase of temperature. The decomposition curve, plotted in the figure, is rather indeterminate but it certainly does not represent the mere dissociation of a hydrate or higher oxide. The peculiar shape of the curve in the neighbourhood of 385° was due to a sudden decomposition, followed by rapid absorption of part of the gaseous products. A portion of the gas was analysed and proved to be a mixture of equal volumes of nitrogen and nitrous oxide. As water also appeared to be produced by the decomposition, a determination of water was carried out on a further sample. The full analysis was Cr, 61·2; N_2, 3; N_2O, 4·5; H_2O, 2; O_2 (by diff.), 29·3%. In spite of its apparent homogeneity, it thus seems extremely doubtful if this powder is a true compound, and it certainly does not possess any of the simple formulæ given to it by the previous workers. It is probably a solid solution of two or more compounds or else a surface compound.



A further point of interest concerns the solid product of decomposition of ammonium dichromate at higher temperatures, usually assumed to be chromic oxide. Other workers have commented on the heterogeneous appearance of this material, which usually consists of dark olive-green flakes mixed with a smaller amount of a black substance. On heating the black powder discussed above, an olive-coloured product was obtained. This was analysed for chromium; the results tabulated below show (No. 1) that the percentage of chromium is below that corresponding to chromic oxide. Prolonged ignition only increased this percentage slightly.

No.	Oxide.	Cr, %.
1	Residue of ignition of black powder at 350°	67·3 ± 0·5
2	Olive-green and black oxide obtained by heating ammonium dichromate in air in the Bunsen flame	67·5 ± 0·4
3	No. 2 heated strongly over Meker burner	67·8
4	No. 2 reduced in hydrogen for 2 hrs. at 750°	67·6
5	No. 2 „ „ „ 4 hrs. at 750°	68·1
6	No. 2 „ „ „ 21 hrs. at 800°	68·4
7	Chromic oxide formed by heating mercurous chromate	68·4

An analysis was then made of the olive-green and black residue formed by the direct decomposition of ammonium dichromate at atmospheric pressure. The results (No. 2) show that this also is not pure chromic oxide. At first it was thought that this residue was a mixture of two compounds, the olive chromic oxide together with small quantities of a black higher oxide. A quantity of the black flakes was therefore separated mechanically from the main bulk. These were extraordinarily porous but underwent no decomposition below 800° although the colour changed to olive-green in the process. The black compound was thus probably another modification of chromic oxide.

Reduction of the olive-green oxide took place only slowly in hydrogen, but after 21 hours at 800° there was complete transformation into chromic oxide. It was noticed that, after reduction, the voluminous olive-green powder had changed into a compact bright green powder similar in appearance to chromic oxide prepared by ignition of chromic anhydride or mercurous chromate.

From these data it may be concluded that the olive-green oxide resulting from the decomposition of ammonium dichromate is an oxide of chromium containing rather more oxygen than is required by the formula Cr_2O_3. This excess of oxygen may be present as a surface oxide, but the difficulty of reduction and other considerations tend to indicate that it is a non-stoicheiometric compound.

EXPERIMENTAL.

Decomposition of Ammonium Dichromate in a Vacuum.—A quantity of powdered ammonium dichromate of tested purity was placed in a small bulb from which a length of wide glass tubing led to a trap filled with tightly packed glass-wool. The system was evacuated by means of an oil-pump, and the dichromate heated. Explosive decomposition of the salt took place, and the solid product, a voluminous black powder, was ejected into the trap, the pump being kept running during the reaction. The product was well washed with water to free it from undecomposed ammonium dichromate, a precaution apparently neglected by most of the earlier workers, and dried by heating at 150°. Analysis of this compound was rather difficult since it tended to decompose slightly while still moist. The chromium analysis quoted (No. 1) is the mean of six determinations.

Analysis of the Olive-green Oxide.—The results quoted in the table were obtained by volumetric analysis of the dichromate formed by fusion of the oxide with sodium peroxide. The result (No. 2) is the mean of 8 determinations and was also checked by gravimetric analysis in which a known weight of the pure ammonium dichromate was ignited and the residue weighed.

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