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THE INTERCONVERSION OF ORTHORHOMBIC CHROMIUM OXY-HYDROXIDE AND CHROMIUM DIOXIDE

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The thermal behaviour of CrOOH and CrO_2 in different atmospheres has been studied by means of DTA, TG and X-ray diffraction. The easy interconversion between the two substances at one atmosphere pressure is explained on the basis of the results obtained.

Recent investigations of the bulk and surface properties of chromium oxide gels [1, 2] have revealed the formation of the orthorhombic CrOOH and the ferromagnetic CrO_2 in certain cases of gels calcined under hydrothermal and oxidising conditions [3]. Tombs et al. [4] established that "pure" CrO_2 is obtained when the orthorhombic form of CrOOH is calcined in air at about 350°; they also reported that the reverse hydrothermal reaction only occurs under pressure at a temperature of about 450°. A clear understanding of the nature of the oxidation–reduction processes involved in the interconversion of CrOOH and CrO_2 is so far lacking and it was considered that further progress could best be made by the application of a number of techniques (DTA, TG and X-ray diffraction).

Three different structures of chromium oxy-hydroxide have been identified: red rhombohedral α-CrOOH [5, 6, 7], green γ-CrOOH [8, 9] (similar to boehmite) and green orthorhombic CrOOH [4, 10]. The colour of such materials may be deceptive because it is influenced by the change of particle size and/or the presence at the surface of chromium in different oxidation states. DTA has been used in a number of investigations of chromium oxide gels [2, 11], but few thermal studies have been made of the decomposition of the well-defined oxides or hydroxides. A blue-grey CrOOH (probably essentially α-CrOOH) was found to undergo an endothermic change at 450° [12], which was associated with the crystallization of α-Cr_2O_3. The thermal decomposition of the orthorhombic CrOOH does not appear to have been studied by DTA, but the transformation of CrO_2 to α-Cr_2O_3 has been reported [11, 13–16] to occur at about 420°.

Experimental

The samples of CrOOH and CrO_2 were supplied by the RCA Laboratories, U.S.A. No impurities could be detected by X-ray diffraction. DTA experiments were performed on a Stanton Standata apparatus, model 625, in still air, dynamic vacuo (0.1 mm Hg) and dynamic atmospheres [1000 cm^3(stp)/min] of pure oxygen, nitrogen or hydrogen. α-Al_2O_3 was used as the reference solid and the rate of heating was standardized at 10°/min. Our previous work on these materials had demonstrated that a variation in the rate of heating, within the range 4°/min – 10°/min, had very little effect on the DTA curve. In each run, 100 mg of sample and of reference material were placed in cylindrical platinum crucibles (diam. = 6 mm, height = 8 mm) which were mounted on the top of the two Pt-PtRh thermocouples inside the vertical cylindrical furnace.

A Stanton TR01 thermobalance was used for the thermogravimetry. 120 mg of sample was placed in a shallow alumina crucible (5 cm^3) mounted on a platform inside the vertical cylindrical furnace within 2 cm of the Pt-PtRh thermocouple. The heating rate was 3°/min and corrections were made for buoyancy. X-ray powder photographs were obtained using a Philips 11704 X-ray unit (Cu Kα radiation) and a powder camera of 117.83 mm diameter.

Results and discussion

I. *CrOOH.* The DTA curves for the decomposition of the orthorhombic CrOOH are shown in Fig. 1. In air (Fig. 1a), the thermal decomposition occurred in three stages: a broad exotherm around 250°, a pronounced endotherm at 480°,

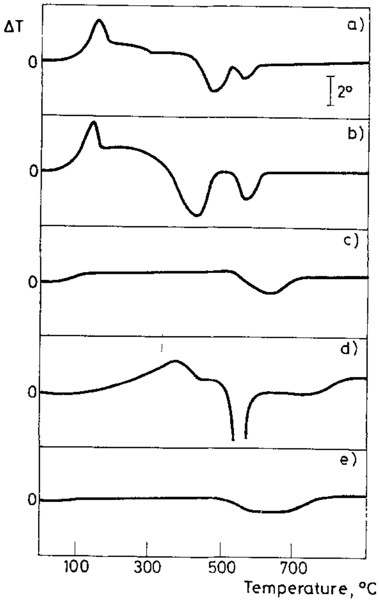

Fig. 1. DTA curves of CrOOH; 10°/min: a) air, b) oxygen, c) nitrogen, d) vacuo, e) hydrogen

and a smaller endotherm at 550°. The results of the DTA experiments conducted in oxygen, nitrogen, vacuo and hydrogen (Fig. 1b, c, d and e respectively) together with the X-ray powder patterns of the intermediate products provided a basis for the elucidation of the mechanism of the thermal decomposition.

The first exothermic reaction was enhanced in oxygen, but was suppressed in both nitrogen and hydrogen. In vacuo the exotherm was delayed until a temperature of about 365°. In air no change in crystal structure could be detected, but after heating to 400° in oxygen the strongest lines of CrO_2 were apparent in addition to the CrOOH pattern. In the latter experiment, the sample became nearly black in colour. These results suggest that the 250° exotherm corresponds to decomposition and oxidation of some CrOOH to CrO_2 – probably in the surface layer.

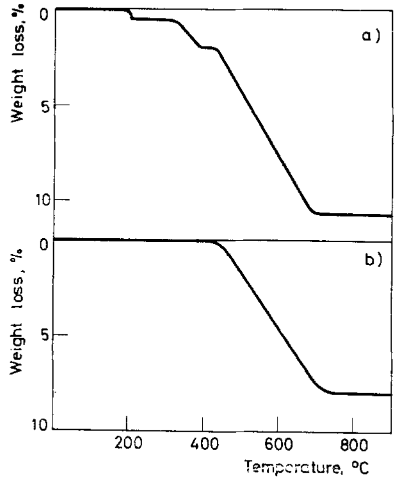

Fig. 2. TG curves for a) CrOOH, b) CrO_2 in air; 3°/min

The 480° endotherm in air resulted in the formation of CrO_2 with some Cr_2O_3. In oxygen, this endotherm was enhanced and was obtained at 425°; the product was now CrO_2, with no detectable Cr_2O_3. The endotherm was absent in an inert or reducing atmosphere and the original orthorhombic structure remained unchanged until the temperature approached 600°.

The decomposition of CrO_2 to α-Cr_2O_3 caused the second endotherm at 550° in air and oxygen. In vacuo the endotherm was very pronounced, whereas in nitrogen and hydrogen it was broadened, reduced in intensity and delayed until about 600°, when the conversion of the CrOOH to α-Cr_2O_3 occurred.

The thermogravimetry was carried out at a relatively slow rate of heating. Three stages of weight loss were observed (Fig. 2a), but they occurred at lower temperatures than the corresponding DTA peaks. The first weight loss, of about

0.5%, occurred between 190° and 210°. The second, of about 1.4%, was observed between 310° and 400° and corresponded approximately to that required (1.2%) for the reaction

$$2\,CrOOH + 1/2\,O_2 \rightarrow 2\,CrO_2 + H_2O$$

The third stage, between 420° and 700°, involved a weight loss of 8.7% as compared with 9.6% required for the reaction

$$2\,CrO_2 \rightarrow Cr_2O_3 + 1/2\,O_2$$

It may be noted that the total weight loss was 10.5%, in excellent agreement with 10.6% demanded for the overall reaction

$$2\,CrOOH \rightarrow Cr_2O_3 + H_2O$$

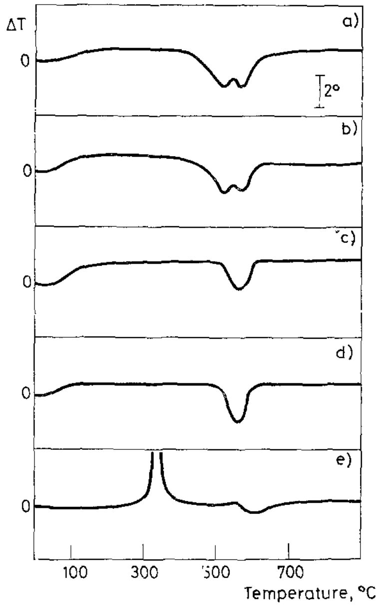

Fig. 3. DTA curves of CrO_2; 10°/min: a) air, b) oxygen, c) nitrogen, d) vacuo, e) hydrogen

II. *CrO_2*. The DTA curves obtained with the sample of CrO_2 are shown in Fig. 3. The twin endotherms obtained in air and oxygen (Fig. 3a and b) indicated that the decomposition occurred in two stages – at temperatures of 507° and 560°. X-ray diffraction revealed that the first stage did not produce any detectable change in the crystal structure, whereas the second led to a rearrangement of the lattice to the stable α-Cr_2O_3.

The decomposition of CrO_2 in nitrogen (Fig. 3c) involved only one endotherm, at 510°. Similarly, in vacuo (Fig. 3d) only one endothermic peak was registered, at 560°. These results suggest that the tetragonal CrO_2 (rutile) structure is stabilised to some extent in an oxidising atmosphere.

The DTA curve obtained in hydrogen (Fig. 3e) is especially interesting. The large exothermal peak around 330° corresponded to the quantitative reduction of CrO_2 to the orthorhombic CrOOH, characterised by X-ray diffraction. The CrOOH so formed was reconverted by heat treatment in air (at about 480°) or in oxygen (at 400°) to CrO_2. We may therefore summarise the interconversion of CrOOH and CrO_2 under one atmosphere pressure by means of the equation

$$\mathrm{CrOOH} \underset{H_2\,(330^\circ)}{\overset{\text{Air }(480^\circ);\ O_2\,(400^\circ)}{\rightleftarrows}} \mathrm{CrO_2}$$

Continuation of the DTA of CrO_2 in hydrogen above 330° resulted in the conversion of the CrOOH to Cr_2O_3 at 605°. If the reduction in hydrogen was carried out after some decomposition of CrO_2 to Cr_2O_3 had occurred, the product was impure, being then a mixture of CrOOH and Cr_2O_3.

Thermogravimetry gave only one step for the decomposition of CrO_2 in air (Fig. 2b), the weight loss of ca. 8% occurring between 430° and 740°. From the TG curve we have estimated the activation energy as 25.5 kcal/mole and the pre-exponential factor as 1, by the method of Freeman and Carroll [17].

The easy interconversion of orthorhombic CrOOH and tetragonal CrO_2 can be explained on the basis of the close similarity of their structures. Thus, the dimensions of the unit cells are as follows:

Orthorhombic CrOOH [10]	Tetragonal CrO_2 [18, 19]
$a = 4.861$ Å	$a = 4.421$ Å
$b = 4.292$ Å	
$c = 2.960$ Å	$c = 2.918$ Å
$\rho = 4.5$ g/cm^3	$\rho = 4.0$ g/cm^3

The introduction of H atoms into the rutile CrO_2 structure allows the formation of hydrogen bonds between the CrO_6 octahedra in one plane, i.e. between central octahedra and corner octahedra, but the overall crystalline structure is only slightly deformed as indicated by the values of the unit cell parameters. On the other hand, the rhombohedral corundum structure of α-Cr_2O_3 is much more compact ($\rho = 5.21$ g/cm^3) so that hydrogen atoms are not able to force an entry into the lattice and therefore Cr_2O_3 cannot be converted into CrOOH.

It is interesting to note that the DTA curves reported here for CrOOH and CrO_2 are quite different in character to those obtained earlier with hydrous chromium oxide gels. Thus, the pronounced exotherm associated with the glow phenomenon has not been observed in the course of transformation of CrO_2 to α-Cr_2O_3. This may appear surprising in view of the appreciable oxidation which precedes the glow exotherm when chromium oxide gels are heated in oxygen.

It seems likely then that even under the most favourable conditions, the formation of CrOOH and CrO_2 is restricted to a small proportion of the gel.

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Résumé — Étude du comportement thermique de CrOOH et de CrO_2 dans différentes atmosphères, par ATD, TG et diffraction de rayons X. Interprétation de l'interconversion légère entre les deux substances sous une pression d'une atmosphère.

Zusammenfassung — Es wurde das thermische Verhalten von CrOOH und CrO_2 in verschiedenen Atmosphären mit Hilfe der Differentialthermoanalyse, Thermogravimetrie und Röntgendiffraktion untersucht und auf Grund der Ergebnisse die leichte Umwandlung zwischen den zwei Verbindungen unter 1 Atm. Druck erklärt.

Резюме — Термическое поведение CrOOH и CrO_2 при различном давлении изучено с помощью ДТА, ТГ и рентген-дифракции. На основании полученных результатов объяснены небольшие превращения, происходящие между этими двумя веществами при данном давлении.