Thermochimica Acta, 54 (1982) 319–325
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

INFRARED ABSORPTION OF CHROMIUM TRIOXIDE AND ITS SUBOXIDES

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(Received 26 October 1981)

ABSTRACT

The chromium oxides, obtained by the thermal decomposition of chromium trioxide, presented a bewildering array of possible mixed valency compounds. The IR absorption measurements in the range 400–5000 cm^{-1} revealed the presence of the valencies +6, +5, +4, +3 in the samples between CrO_3 and Cr_2O_3.

INTRODUCTION

It is known that the IR region of the spectrum can yield valuable information on the low energy characteristics of the oxides. These characteristics may arise due to well-defined vibrational states as a molecular metal–oxygen stretching frequency, as a result of lattice dispersion, or due to impurity excited or trapping states. Thus the IR absorption of the CrO_3 and the Cr_2O_3 oxides had been previously tackled by several authors [1–19]. For the sake of brevity these are summarized in Table 1, together with the present data. Most of the previous work was restricted to definite compounds which had stable formulae such as CrO_3 [2–10,12,15,16,18], CrO_2 [13,14,17,19] and Cr_2O_3 [1,2,7–9,15].

As far as the authors are aware there is no mention in the literature concerning the IR of the phases formed between CrO_3 and Cr_2O_3. The only mention is that of Shopov and Palazov [11] for $CrO_{2.906}$ and the bands approached more or less those of CrO_3, namely at 950, 908 and 888 cm^{-1}.

In the present work the IR spectra of a number of oxides in the range CrO_3–Cr_2O_3 system have been investigated as part of a general program to indicate, as nearly as possible, the significant correlations and the sensitivity of the technique to changes in the oxidation states of the compounds when passing from CrO_3 to Cr_2O_3.

EXPERIMENTAL

The starting material for preparing this series of oxides was CrO_3 (Merck). Certain compositions were chosen to represent the stable steps or decomposition

TABLE 1

The IR data for Cr_2O_3 and CrO_3

Ref.	CrO_3 peak position (cm^{-1})	Cr_2O_3 peak position (cm^{-1})
This work	890, 904, 952	400, 439, 545–565, 598, 635, 655
1		658 (s), 1111 (w)
2, 8	904, 950 (valence vibration)	412, 448, 590, 630, 650, 690
3	472, 910, 946	
6, 12	893 (Cr–O–Cr) 969 (Cr–O) free	
7	588–625 (w b) 729 (w), 971 (s)	578 (s), 641 (s) 690 (w)
9	no bands (240–700)	407 (w), 435 (w), 555 (s), 625 (s)
10	451, 530, 730, 795, 872, 940	
4, 5	971 (the symmetrical chromate ion produced by atmospheric H_2O) 952 (asymmetric CrO_3 stretch) 797 (Cr–O–Cr asymmetric stretch)	
18	CrO_3 (vapour) 995 (Cr–O), 850 (Cr–O–Cr), 485, 350	

products of CrO_3 at different temperatures, according to the studied TGA. The temperatures of the preparations were chosen at temperature regions before every change, whatever the change. The method of Costea [20] was applied in the present investigation using the thermal decomposition of CrO_3 at different controlled temperatures to ±3°C in a silica crucible.

The composition of all samples illustrated in Table 2 was confirmed by chemical

TABLE 2

Composition of chromium oxide samples

Cr-oxide	Preparation temp. (°C)	Time (h)
CrO_3	Starting material dried at 100°C under vacuum	2
$CrO_{2.988}$	227	3
$CrO_{2.71}$	287	6
$CrO_{2.41}$	290	6
$CrO_{2.399}$	350	3
$CrO_{2.3}$	350	4
$CrO_{1.66}$	380	6
$CrO_{1.516}$	450	6

analysis, ignition loss and X-ray analysis. The X-ray analysis indicated the presence of more than one phase.

The IR absorption of the above samples was measured at room temperature from 400 to 5000 cm^{-1}. Pellets were made to constant known concentration by weight and were run against KBr blanks. Only in the case of CrO_3, was there evidence of the occurrence of redox. This could be minimized by suitable precautions, especially by excluding water. The spectra were recorded employing Beckman instrument GMBH München-Bel Nachbestellung Kat. Nr. 914539 Angeben. The signal-to-noise ratio was improved by adjusting suitable conditions of slit program, recording scale, recording speed, amplification, etc., which were kept constant to the same setting throughout all measurements. Mechanical scattering from the powdered samples had been rather minimized by sieving all samples from the same 0.2 mesh.

RESULTS AND DISCUSSION

A discussion of the mixed valence compounds of chromium is hampered by the fact that this element can assume integral valencies from +1 to +6. The IR spectra

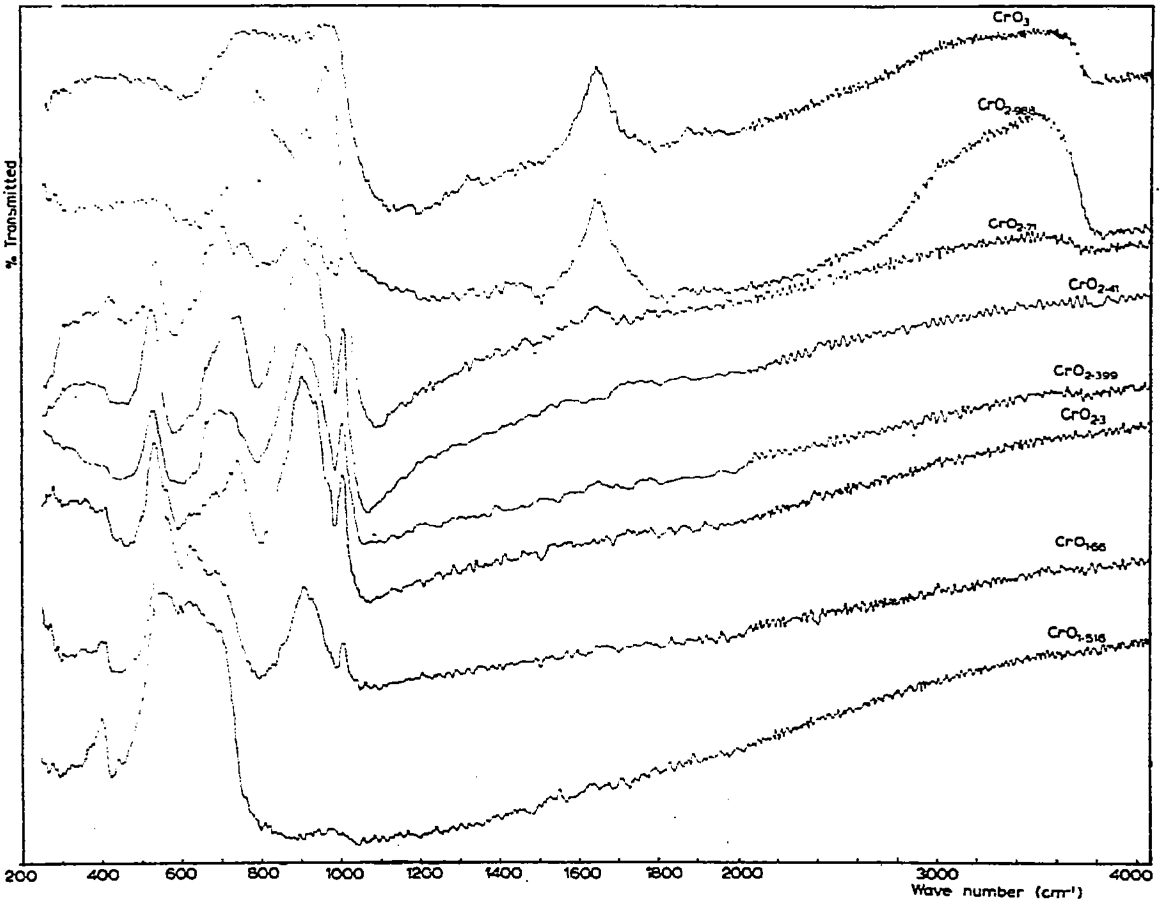

Fig. 1. The IR absorption spectra of all the chromium oxide samples.

of chromium oxide samples between CrO_3–Cr_2O_3 are represented in Fig. 1. Gradual variation in the spectra of some samples is revealed with respect to the broadening, sharpness and intensity of the bands. Additional bands are detected for the oxides in between while some bands totally disappeared in the latter oxides. Thus one would be able to follow at least qualitatively the modifications which result during the ignition of CrO_3 in the studied products.

For the sake of brevity and simplicity of the discussion and comparison with previous data, the obtained absorption bands and those of the previous authors are tabulated in Tables 1 and 3, respectively. Thus the first spectrum which corresponds to CrO_3 (Merck) shows a very broad band covering the range 700–980 cm^{-1}. It is well known that CrO_3 is highly hygroscopic, so in spite of the drying the 800–1100 cm^{-1} OH bending region stated by Zecchina et al. [21] circumvents those characteristic of CrO_3. The presence of water is more clear at 1620 and 3000–3700 cm^{-1} for OH stretching regions.

The second spectrum for $CrO_{2.988}$ is more representative of the spectrum of CrO_3. There are three bands at 890, 904 and 952 cm^{-1} which characterize the Cr^{6+} as

TABLE 3

Peak positions for the different chromium oxide samples

Wave No.	400–500 cm^{-1}			500–600 cm^{-1}		600–700 cm^{-1}				
CrO_3										
$CrO_{2.988}$										
$CrO_{2.71}$	407, sho.	415, sha.	485 w.	534 sha.s.		615 sho.	626 sho.	656 sha. w.	663 sho.	695 sha. m.
$CrO_{2.41}$	405 v.w.			525 sha.s.		620	655,	668, sho.	690 Br. w.	
$CrO_{2.399}$	407			520 sha.s.		612, sho.	629, v.w.	655 sho.		
$CrO_{2.3}$	408	440–447	471	527 sha.s.	555 sho.	616, w.	627, v.w.	650, sho.	682 w.	
$CrO_{1.66}$	410 Br.s	442 v.w.	475 w.		558 564 568	618, m.	629, sho.	645, sho.	680 w.	
$CrO_{1.516}$	400 sha.s.	439 sha.m.		545–565 Br.s.	598	618, Br.	635, w.	655, v.w.	678 v.w. 694 s.	

s = strong; m = medium; w = weak; vw = very weak; sho = shoulder; sha = sharp; Br = broad.

sharp and strong ones. The latter two bands were obtained by Dupuis [3] at 910 and 946 cm^{-1}. Barraclough et al. [6] observed two bands at 893 and 969 cm^{-1}. The band at 969 cm^{-1} was considered to represent the stretching frequency of the two free Cr–O groups, while the much broader band at 893 cm^{-1} represents the vibration of the continuous Cr–O–Cr chain of the distorted CrO_4 tetrahedra. This band was stated by Camelot [16] for CrO_3 at 890 cm^{-1}. Duval et al. [8] observed two bands, 904 and 950 cm^{-1} for commercial CrO_3 and for that ignited till 285°C without loss of weight. Shopov and Palazov [11] observed the same three bands at 882–888 and 950 cm^{-1} for the composition $CrO_{2.906}$. These results of Shopov and Palazov [11] and Duval et al. [8] favour the present resemblance in the spectra of the two samples for the CrO_4 tetrahedra observed from X-ray [22,23].

The bands observed at 780 and 795 cm^{-1} could be attributed to impurities or some polarization as stated by Duval et al. [8]. These bands are more probably due to water molecules especially since they are refined in the sample of $CrO_{2.988}$ and disappeared totally with the disappearance of the water peak at 1620 cm^{-1} in the spectra of the following samples.

Heating CrO_3 to 278°C leads to a new spectrum No. 3. The vibrations of the

700–800 cm^{-1}			800–900 cm^{-1}				900–1000 cm^{-1}		
		780					910	952	
		783 sha.s 795 sho.w.				890 m	904 sha. m.	952 sha. m.	
716, Br.	740	755	820 w.	840 v.w.	878 sha.	893 sha.	933 sha. m.	967 sha. m.	993 sha. s.
718 sho.				842		890 Br.s.			991 sha.s
705, sho.	720–738 Br.s.			845 sho.		892 Br.s.		960 w.	993 sho.
705,	716, sho.	733 sha.s.				894 sha.s.	930 sho.	960 sho.	994 sha.s.
700 sho.						894 sha.s.	903 918		995

hexavalent CrO_3 at 904 and 952 cm^{-1} totally disappeared while it was still contaminated with other valencies. The bands at 893 and 967 cm^{-1} stated by Barraclough et al. [6] are still preserved together with other bands representing lower valencies. Thus the bands at 878, 933 and 993 cm^{-1} which are stated by Duval et al. [8] to be at 880, 930, 961 and 985 cm^{-1} indicate the appearance of CrO_2 and the modification of the structure of CrO_3.

Considerable changes are produced in the low frequency range. The bands at 407, 626, 656, 695 are stated to represent the appearance of Cr_2O_3 as is obviously clear from Table 1. The valency +5 was stated by Lorthioir and Michel [24] to be the least known state of Cr and it might be present in CrF_5. Comparing the bands at 485, 668, 716 and 755 cm^{-1}, which are not present in the first two spectra, by those observed by Steven and Loehr [25] for the chromium pentafluoride at 475, 670, 715 and 755 cm^{-1} either by IR or Raman spectra, the bands at 534 and 740 cm^{-1} may also be taken as an indication of the presence of the pentavalent state. This may be liable to be present from the X-ray diffraction lines of the investigated samples.

However, Cr_2O_5 and Cr_5O_{12} were stated by Glemser et al. [26] to be identical and Cr_5O_{12} was stated by Wilhelmi [27] to contain chromium as hexavalent and trivalent atoms. Also Lorthioir and Michel [28] did not find any evidence for the Cr^{5+} throughout the thermal decomposition products of CrO_3.

The spectra of the samples in between (Nos. 4–7) contain numerous bands and represent the different valencies of chromium. The valency +6 is still preserved by the appearance of the band at 890 cm^{-1}. The valency +3 is clear by the appearance of the Cr_2O_3 bands namely at 400, 439, 545–565, 618, 635, 655 and 694 cm^{-1}. The valency +4 is clear by the appearance of the bands of CrO_2. Thus the bands at 878, 933, 967 and 993 cm^{-1} are stated by Duval et al. [8] to be at 880, 930, 961 and 985 cm^{-1} and are due to CrO_2.

Thus there still remains an ambiguity with regard to the presence of the valence +5 in the samples. This is to be investigated later through the magnetic properties of this series of samples. It is likely that the low frequency bands are various Cr–O deformations but their symmetry species are unknown.

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