

# Phthalic Acid as a Reagent in Inorganic Qualitative Analysis of Metal Ions. Part. II. Thermogravimetric, Differential Thermal and Infrared-spectral Studies of Iron(III), Chromium(III), and Aluminium(III) Compounds Precipitated with Hydroxyl and Phthalate Ions and of Potassium Biphthalate

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Precipitates were formed when 2 M sodium hydroxide and 0.5 M potassium biphthalate solutions were added to 100 ml of 0.01 M iron(III) chloride, chromium(III) chloride, or aluminium(III) chloride solutions. These, after drying in air and in a desiccator, had the compositions  $\text{Fe}_3\text{O}_5(\text{OH})_5(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ ,  $\text{Cr}_3(\text{OH})_{12}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , and  $\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , respectively. If 0.5 M potassium biphthalate only was added to the iron(III) chloride solution, the precipitate formed had the composition  $\text{Fe}_2(\text{OH})_2[(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2\text{H})]_2$ . With 2 M sodium hydroxide solution, the hydroxides  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3 \cdot 1.75\text{H}_2\text{O}$  and the oxyhydrate  $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  were formed. The TG and DTA curves and IR spectra of the compounds and potassium biphthalate were recorded and the results are discussed.

In the qualitative analysis system which was described in the first part of this series<sup>1</sup> and is being used in our inorganic chemistry teaching laboratory, the division of the metal ions into analytical groups is to a certain degree based on the adjustment of the pH of the solutions studied. In the analytical scheme, the cation group II is precipitated with sodium hydroxide from the solution buffered with potassium biphthalate. The pH of the solution is in this way held between 4 and 5. The cation group II consists of the following ions: tin(II), tin(IV), antimony(III), bismuth(III), iron(II), iron(III), chromium(III), and aluminium(III).

According to the values of the solubility products taken from the literature,<sup>2</sup> the hydroxides of these metals begin to precipitate from 0.01 M solutions of the metal salts at roughly the following pH's at room temperature (25°C):

tin(II) hydroxide ( $pK_{s,0}=25.0-25.7$ ) at pH 2.3 and tin(IV) hydroxide ( $pK_{s,0}=56$ ) at pH 0.5. The tin(II) ion is usually oxidized in the solution to the tin(IV) ion, and precipitated as this. The antimony(III) hydroxide ( $pK_{s,0}=41.4$ ) precipitates at pH 1, but is immediately converted to the basic salt  $SbOX$ , where X may be  $Cl^-$ ,  $NO_3^-$ , etc., depending on the solution. Bismuth(III) hydroxide ( $pK_{s,0}=30.4$ ) precipitates at pH 4.6, but changes immediately to the  $BiOX$  salt. The compounds mentioned have such low solubility products that they are almost completely precipitated from the solutions at pH 5.

The iron(II), iron(III), chromium(III), and aluminium(III) ions form an interesting quartet because they are strongly complex-forming ions and additionally their hydroxides are precipitated near the pH range which divides the metal ions into different analytical groups. Iron(II) hydroxide ( $pK_{s,0}=14.0-15.1$ ) precipitates at about pH 7.7, but iron(II) ions are easily oxidized by air in the solutions and therefore precipitate as iron(III) hydroxide. Iron(III) hydroxide ( $pK_{s,0}=36.4-39.4$ ), chromium(III) hydroxide ( $pK_{s,0}=29.8-30.8$ ), and aluminium(III) hydroxide ( $pK_{s,0}=31.7-33.5$ ) are precipitated in the conditions described above at about the pH values 2.1, 4.6, and 3.8, respectively.<sup>2</sup>

In the light of this examination, the metal ions of the cation group II with the precipitation conditions used in the qualitative analysis scheme<sup>1</sup> would precipitate as hydroxides, hydroxy hydrates or basic phthalates. The basic phthalate, however, was formed only with iron(III) and chromium(III) ions and, with the latter ions only when sodium hydroxide was also added to the solution. This may be seen from the following comparison of precipitation conditions and the composition of the precipitates.

## EXPERIMENTAL

*Preparation of the compounds.* The compounds studied were precipitated in three ways, by adding to 100 ml of 0.01 M iron(III), chromium(III), or aluminium(III) chloride solutions: (1) according to the analytical scheme,<sup>1</sup> 0.5 M potassium biphthalate and 2 M sodium hydroxide solutions, or (2) a 0.5 M potassium biphthalate solution, or (3) a 2 M sodium hydroxide solution. The precipitation method is indicated by the symbols (I), (II), or (III) after the chemical formulas of the compounds.

The precipitations were performed at room temperature, after which the samples were warmed for 10 min in a water bath at 90–95°C. They were then cooled to room temperature, filtered and washed with water. The precipitates were allowed to dry in the air for a day, and for two weeks in a silica gel desiccator at room temperature. The results of the experiments are shown in Table 1.

The micro combustion analyses of the phthalate complexes gave the following results:

Complex	Precipitation method	Found		Analysis formula	Calcd	
		C	H		C	H
Iron	I	19.59	1.77	$C_8H_9O_{14}Fe_3$	19.35	1.83
Iron	II	40.52	2.45	$C_8H_6O_5Fe$	40.38	2.54
Chromium	I	18.19	2.91	$C_8H_{16}O_{16}Cr_3$	18.33	3.08

*Apparatus and measurements.* The TG analyses were performed with a Fisher TGA System Series 100. The recorder was a two pen type Hewlett Packard model Moseley 7100 BM. About 7–9 mg samples were used with a platinum pan and static air conditions. The rate of heating was 10°C/min.

Table 1. The results of the precipitation experiments.

Precipitation method	Precipitate colour	Precipitate colour	Precipitate colour
I	Brown	Dark green	White
II	Light brown	No	No
III	Dark brown	Green	White
Metal ion	$\text{Fe}^{3+}$	$\text{Cr}^{3+}$	$\text{Al}^{3+}$

The DTA analyses were made with a Fisher DTA System Series 200 A, the recorder being the one mentioned above. The differential thermocouple was the "Platinel I" of the equipment. As reference compound, aluminium oxide, "Alumina", from the Fisher Scientific Co. was used. The reference was dried at 600°C and then kept in a silica gel desiccator. The samples were from 30 to 40 mg and the heating rate was 10°C/min.

The IR spectra were run on a Perkin Elmer Model 457 spectrophotometer. Potassium bromide disks were used, consisting of 1 mg of the sample per 300 mg of potassium bromide. Potassium bromide was a guaranteed reagent "Uvasol" from E. Merck AG. Before use, the reagent was first sieved (mesh diameter 0.044 mm) and then dried at 120°C.

*Reagents.* The guaranteed reagents of E. Merck AG were used.

## RESULTS AND DISCUSSION

The thermograms of the compounds studied are shown in Fig. 1, and the detailed analysis of the curves in Table 2. The DTA curves are seen in Fig. 2 with the peak temperatures and their assignments in Table 3. The IR spectra are represented in Fig. 3 and the absorption bands with their assignments in Tables 4–6.

*Potassium biphthalate.* The thermal decomposition of potassium biphthalate is thought to occur in two main stages which are independent of the decomposition atmosphere. Firstly, dipotassium phthalate is formed by volatilization of phthalic anhydride and water, and secondly, dipotassium phthalate is decomposed to give potassium carbonate and volatile products.<sup>3–7</sup> The initial decomposition temperature for potassium biphthalate found by different workers varies from 145°C<sup>7</sup> to 240°C,<sup>6</sup> depending on the decomposition conditions and the heating rate. The decomposition and sublimation temperature in static air, 228°C, observed in this study (Fig. 1, curve 1 and Table 2) is well within this range. Further observations of the decomposition processes from the thermogravimetric curve were impossible because of the strong sublimation effects.

The DTA curve (Fig. 2, curve 1) and peak temperatures (Table 3) reported here may be compared with those of Belcher *et al.*<sup>4</sup> and with their derivative TG curves. Thus, the endothermic peaks at 90°, 125°, and 185°C may be assigned to changes in structure and the melting of potassium biphthalate. The peak at 305°C corresponds to the decomposition of potassium biphthalate, sublimation of phthalic anhydride and removal of water. The endothermic peak at 437°C marks the melting of dipotassium phthalate. The exothermic peaks at 460°, 517° and 540°C are due to the decomposition of dipotassium phthalate and formation of potassium carbonate, and the peaks at 580° and

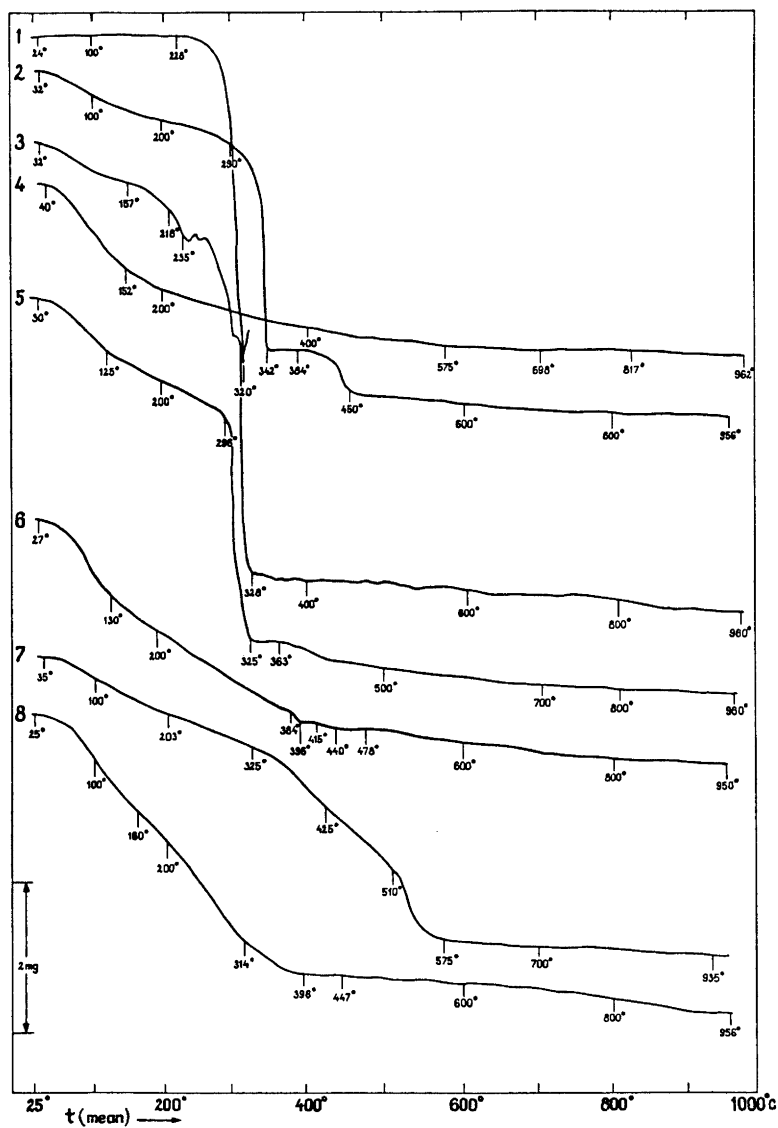


Fig. 1. The thermograms of potassium biphthalate and of the precipitated iron(III), chromium(III), and aluminium(III) salts.

Curve: 1,  $\text{KH}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ ; 2,  $\text{Fe}_3\text{O}_5(\text{OH})_5(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I);  
 3,  $\text{Fe}_2(\text{OH})_2[(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2\text{H})]_2$ , (II); 4,  $\text{Fe}(\text{OH})_3$ , (III);  
 5,  $\text{Cr}_2(\text{OH})_{12}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I); 6,  $\text{Cr}(\text{OH})_3 \cdot 1.75\text{H}_2\text{O}$ , (III);  
 7,  $\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , (I); 8,  $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , (III).

Table 2. The detailed analyses, weight losses and temperature ranges of the thermal processes of the metal salts studied.

Salt	Reaction	Weight loss, %		Temperature range, °C
		Calc.	Found	
KH(O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Decomposition and sublimation	—	—	228—
Fe <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , (I)	Fe <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> → Fe <sub>3</sub> O <sub>7.5</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> + 2.5H <sub>2</sub> O	9.1	10.6	32—290
	Fe <sub>3</sub> O <sub>7.5</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> → Fe <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	32.3	34.2	290—342
	Fe <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> → Fe <sub>2</sub> O <sub>3</sub>	21.6	17.3	384—956
	Yield (%) of Fe <sub>2</sub> O <sub>3</sub> : 48.7 (found); 48.2 (calc.)			
Fe <sub>2</sub> (OH) <sub>2</sub> [(O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (CO <sub>2</sub> H)] <sub>2</sub> , (II)	Fe <sub>2</sub> (OH) <sub>2</sub> [(O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (CO <sub>2</sub> H)] <sub>2</sub> → Fe <sub>2</sub> [(O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] <sub>2</sub>	7.6	6.1	32—157
	Fe <sub>2</sub> [(O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ] <sub>2</sub> → Fe <sub>2</sub> O <sub>3</sub>	63.7	71.1	157—960
	Yield (%) of Fe <sub>2</sub> O <sub>3</sub> : 27.1 (found); 33.6 (calc.)			
Fe(OH) <sub>3</sub> , (III)	2Fe(OH) <sub>3</sub> → Fe <sub>2</sub> O <sub>1.5</sub> (OH) <sub>3</sub> + 1.5H <sub>2</sub> O	12.6	12.5	40—152
	Fe <sub>2</sub> O <sub>1.5</sub> (OH) <sub>3</sub> → Fe <sub>2</sub> O <sub>3</sub> + 1.5H <sub>2</sub> O	14.5	13.9	152—962
	Yield (%) of Fe <sub>2</sub> O <sub>3</sub> : 75.3 (found); 74.7 (calc.)			
Cr <sub>3</sub> (OH) <sub>12</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , (I)	Cr <sub>3</sub> (OH) <sub>12</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> → Cr <sub>2</sub> O <sub>3</sub> ·CrO <sub>3</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> + 6H <sub>2</sub> O	20.6	18.4	30—296
	Cr <sub>2</sub> O <sub>3</sub> ·CrO <sub>3</sub> (O <sub>2</sub> C) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> → Cr <sub>2</sub> O <sub>3</sub> ·CrO <sub>3</sub>	39.4	40.7	296—325
	2Cr <sub>2</sub> O <sub>3</sub> ·CrO <sub>3</sub> → 3Cr <sub>2</sub> O <sub>3</sub> + 1.5O <sub>2</sub>	9.5	16.7	363—960
	Yield (%) of Cr <sub>2</sub> O <sub>3</sub> : 40.4 (found); 43.5 (calc.)			
Cr(OH) <sub>3</sub> ·1.75H <sub>2</sub> O, (III)	2Cr(OH) <sub>3</sub> ·1.75H <sub>2</sub> O → 2Cr(OH) <sub>3</sub> ·0.75H <sub>2</sub> O + 2H <sub>2</sub> O	13.4	13.4	27—130
	2Cr(OH) <sub>3</sub> ·0.75H <sub>2</sub> O → Cr <sub>2</sub> O <sub>3</sub> + 4.5H <sub>2</sub> O	34.8	34.9	130—950
	Yield (%) of Cr <sub>2</sub> O <sub>3</sub> : 56.4 (found); 56.5 (calc.)			
Al <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O, (I)	Al <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·4H <sub>2</sub> O + H <sub>2</sub> O	9.4	9.3	35—203
	Al <sub>2</sub> O <sub>3</sub> ·4H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·3.5H <sub>2</sub> O + 0.5H <sub>2</sub> O	5.2	5.0	203—325
	Al <sub>2</sub> O <sub>3</sub> ·3.5H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·2.5H <sub>2</sub> O + H <sub>2</sub> O	10.9	10.8	325—425
	Al <sub>2</sub> O <sub>3</sub> ·2.5H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·1.5H <sub>2</sub> O + H <sub>2</sub> O	12.3	12.3	425—510
	Al <sub>2</sub> O <sub>3</sub> ·1.5H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> + 1.5H <sub>2</sub> O	21.0	19.5	510—935
	Yield (%) of Al <sub>2</sub> O <sub>3</sub> : 54.2 (found); 53.1 (calc.)			
Al <sub>2</sub> O <sub>3</sub> ·6H <sub>2</sub> O, (III)	Al <sub>2</sub> O <sub>3</sub> ·6H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·4H <sub>2</sub> O + 2H <sub>2</sub> O	17.2	17.1	25—160
	Al <sub>2</sub> O <sub>3</sub> ·4H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·1.5H <sub>2</sub> O + 2.5H <sub>2</sub> O	25.9	25.9	160—314
	Al <sub>2</sub> O <sub>3</sub> ·1.5H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O + 0.5H <sub>2</sub> O	7.0	9.3	314—396
	Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O → Al <sub>2</sub> O <sub>3</sub> + H <sub>2</sub> O	15.0	12.1	447—956
	Yield (%) of Al <sub>2</sub> O <sub>3</sub> : 49.0 (found); 48.5 (calc.)			

636°C correspond to the decomposition of potassium carbonate and formation of potassium oxide.

The infrared spectrum of potassium biphthalate in the region 4000—2000 cm<sup>-1</sup> shows two very weak bands at 2910 and 2460 cm<sup>-1</sup> (Fig. 3, curve 1 and Table 4), which may be assigned to the OH stretching bands of the unionized carboxylic group. This suggests dimerization or polymerization of the salt through the carboxylic groups.<sup>8-15</sup>

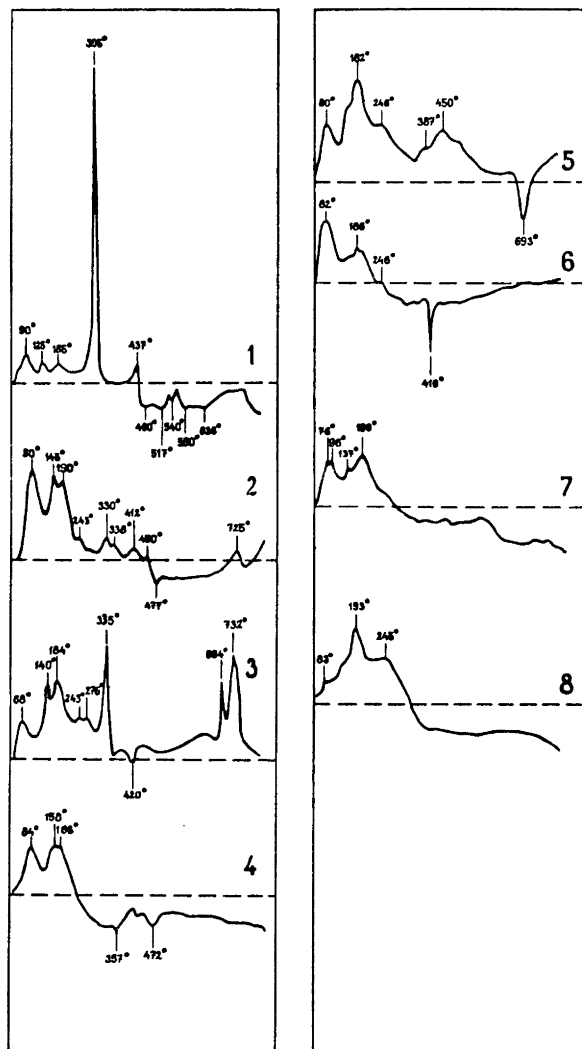


Fig. 2. The differential thermal analysis curves of potassium biphthalate and of the precipitated iron(III), chromium(III), and aluminium(III) salts.

Curve: 1,  $\text{KH}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ ; 2,  $\text{Fe}_3\text{O}_5(\text{OH})_5(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I);  
 3,  $\text{Fe}_2(\text{OH})_2[(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2\text{H})]_2$ , (II); 4,  $\text{Fe}(\text{OH})_3$ , (III);  
 5,  $\text{Cr}_3(\text{OH})_{12}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I); 6,  $\text{Cr}(\text{OH})_3 \cdot 1.75\text{H}_2\text{O}$ , (III);  
 7,  $\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , (I); 8,  $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , (III).

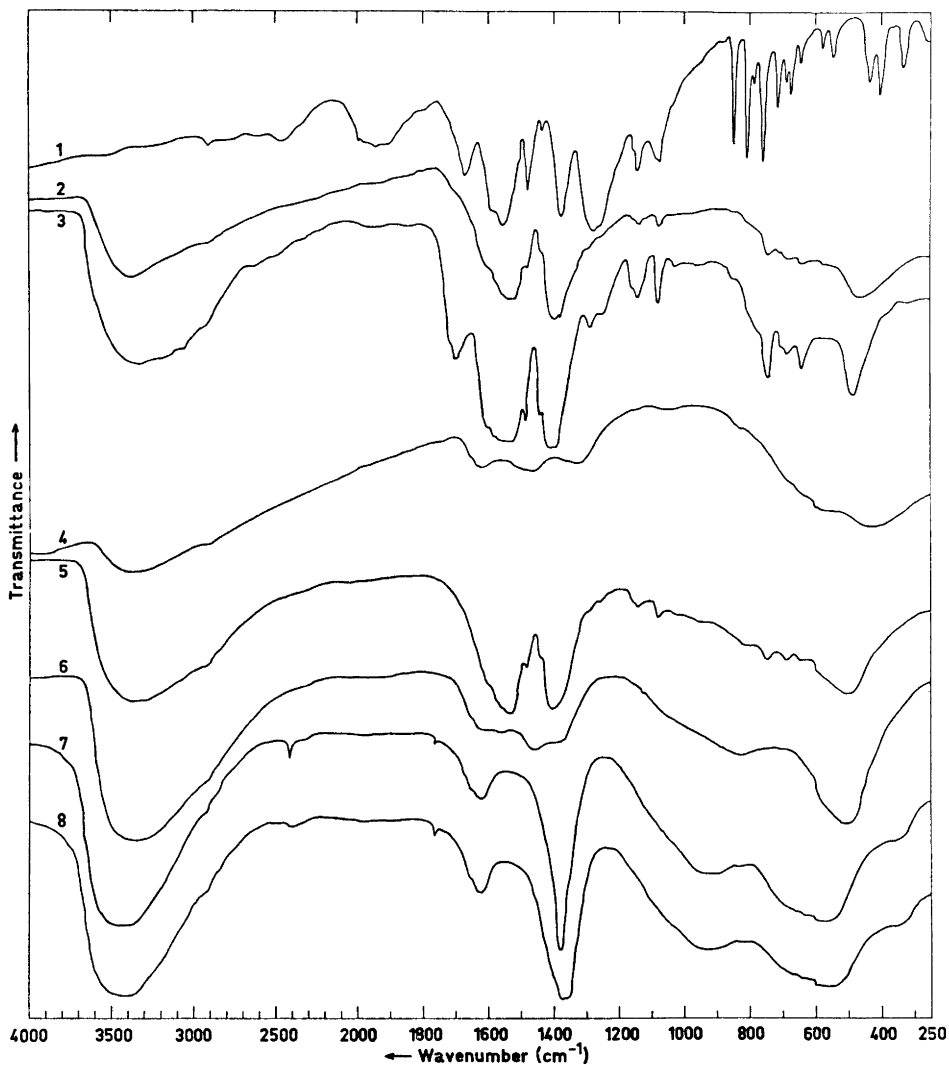
There are several strong bands in the region  $2000 - 1300 \text{ cm}^{-1}$ . The medium and broad band at  $1945 \text{ cm}^{-1}$  is obviously due to the CH out-of-plane bending vibrations of the benzene ring, typical of *o*-disubstituted benzenes.<sup>16-18</sup> The

Table 3. The DTA peak temperatures and their comparison with the TG temperature ranges of the thermal decomposition processes of the metal salts studied.

Salt	Process	DTA peak tem- perature, °C	TG temperature range, °C
$\text{KH}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$	Changes in structure, melting, endoth.	90, 125, 185	24 – 228
	Decomposition, sublimation, »	305	228 –
	Melting of $(\text{KO}_2\text{C})_2\text{C}_6\text{H}_4$ , »	437	
	Decomposition, formation of $\text{K}_2\text{CO}_3$ , exoth.	460, 517 540	
	Decomposition, formation of $\text{K}_2\text{O}$ , »	580, 636	
$\text{Fe}_3\text{O}_5(\text{OH})_5(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I)	Changes in structure, melting, loss of water, endoth.	90, 145, 190, 243	32 – 290
	Decomposition, endoth.	330, 338	290 – 342
	Decomposition, »	412, 450	384 – 450
	Decomposition, formation of $\text{Fe}_2\text{O}_3$ , exoth.	477	450 – 956
	Decomposition, endoth.	725	450 – 956
$\text{Fe}_2(\text{OH})_2[(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2]$ , (II)	Changes in structure, melting, loss of water, endoth.	68, 140	32 – 157
	Decomposition, sublimation, endoth.	184, 243, 276	157 – 328
	Decomposition, endoth.	335	328 – 960
	Decomposition, formation of $\text{Fe}_2\text{O}_3$ , exoth.	420	»
	Decomposition, endoth.	694, 732	»
$\text{Fe}(\text{OH})_3$ , (III)	Changes in structure, loss of water, endoth.	84, 158, 186	40 – 200
	Decomposition, loss of water, formation of $\text{Fe}_2\text{O}_3$ , exoth.	357, 472	200 – 962
$\text{Cr}_3(\text{OH})_{12}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I)	Changes in structure, melting, loss of water, endoth	80, 182, 246	30 – 296
	Decomposition, endoth.	387, 450	296 – 960
	Decomposition, formation of $\text{Cr}_2\text{O}_3$ , exoth.	693	»
$\text{Cr}(\text{OH})_3 \cdot 1.75\text{H}_2\text{O}$ , (III)	Changes in structure, loss of water, endoth.	82	27 – 130
	Decomposition, loss of water, »	186, 246	130 – 384
	Decomposition, formation of $\text{Cr}_2\text{O}_3$ , exoth.	410	384 – 950
$\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , (I)	Changes in structure, loss of water, endoth.	76, 96, 137, 190	35 – 203
	Changes in structure, loss of water, endoth.	83	25 – 160
$\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , (III)	Decomposition, loss of water, endoth.	193, 245	160 – 314

band at  $1668\text{ cm}^{-1}$  is due to the asymmetric CO stretching modes of the unionized carboxylic group, which shows further that the salt is dimerized or polymerized through the carboxylic groups.<sup>8-15,19-28</sup> The intensity of the CO stretching band dominates that of all other double bond bands so that the overtone and combination bands of the substituted benzene ring is masked.<sup>8,16</sup> The low wavenumber of the band also points to internal hydrogen bonding and so to the dimerization or polymerization of the salt.<sup>8-12,19-26</sup>

The strong band at  $1555\text{ cm}^{-1}$  arises from the antisymmetric  $\text{COO}^-$  stretching modes,<sup>23,24,29-33</sup> the medium band at  $1480\text{ cm}^{-1}$  from the CC stretching



*Fig. 3.* The infrared absorption spectra of potassium biphthalate and of the precipitated iron(III), chromium(III), and aluminium(III) salts in the range 4000–250  $\text{cm}^{-1}$  recorded in potassium bromide discs (1 mg of the compound per 300 mg of KBr) at room temperature (about 22°C).

Spectrum: 1,  $\text{KH}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ ; 2,  $\text{Fe}_3\text{O}_6(\text{OH})_5(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I);  
 3,  $\text{Fe}_2(\text{OH})_2((\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2\text{H}))_2$ , (II); 4,  $\text{Fe}(\text{OH})_3$ , (III);  
 5,  $\text{Cr}_3(\text{OH})_{12}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I); 6,  $\text{Cr}(\text{OH})_3 \cdot 1.75\text{H}_2\text{O}$ , (III);  
 7,  $\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , (I); 8,  $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , (III).



Table 4. The wave numbers and assignments of the infrared absorption bands of the precipitated iron(III) salts and of potassium biphthalate.

$\text{Fe}_3\text{O}_5(\text{OH})_5 \cdot \text{O}_2\text{C}_2\text{C}_6\text{H}_4$ , (I)		$\text{Fe}_2(\text{OH})_2 \cdot [(\text{O}_2\text{C})\text{C}_6\text{H}_4(\text{CO}_2\text{H})]_2$ , (II)		$\text{Fe}(\text{OH})_3$ , (III)		$\text{KH}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$		Assignment <sup>b</sup>	Ref.
$\text{cm}^{-1}$	Comments <sup>a</sup>	$\text{cm}^{-1}$	Comments	$\text{cm}^{-1}$	Comments	$\text{cm}^{-1}$	Comments		
380	s, bd	3350	vs, bd	3360	m, bd			$\nu(\text{FeOH}) + \nu(\text{HOH})$	19, 35 45-61, 63, 67, 69
		3050	sh					$\nu(\text{OH})$	10, 61
		2920	sh			2910	vw	$\nu(\text{OH}), (\text{COOH})$	8-15
2900	sh			2900	sh	2460	vw	$\nu(\text{OH}), (\text{COOH})$	8-15
						1945	m, bd	$\pi(\text{CH})$	8, 16-18
		1700	m			1668	m	$\nu_a(\text{OCO}), (\text{COOH})$	8-15, 19-28
				1620	w, bd			$\delta(\text{HOH})$	46, 53, 54-58, 62, 63, 67
1600	sh	1600	sh			1595	sh	$\nu(\text{CO})$ or $\nu(\text{CC})$	14, 17, 20, 23, 24, 26, 31, 32, 34
1530	s	1540	vs			1555	s	$\nu_a(\text{CO}_2^-)$	8, 11, 14, 23, 24, 34, 29, 32, 35
1480	sh	1487	w			1480	m	$\nu(\text{CC})$	8, 14, 16, 17, 34
1438	sh	1440	sh	1465	w, bd	1437	vw	$\delta(\text{FeOH})$ $\nu_s(\text{CO}) + \nu(\text{CC})$	51, 63-71 9-11, 14, 17, 23, 25-27, 29, 32
1400	s	1400	vs					$\nu_s(\text{CO}_2^-) +$	8, 11, 14, 17, 19, 20, 23-27
1380	sh					1377	s	$\nu(\text{CC})$	32, 33, 35
1290	sh	1290	w	1330	w, bd	1278	s	$\delta(\text{FeOH})$ $\nu_s(\text{CO}) + \delta(\text{OCO})$	51, 63-71 9, 10, 20, 23, 25-27, 35
1260	sh	1250	sh			1257	sh	"	25, 33
1140	vw	1145	m			1144	w	$\delta(\text{OH})$	13, 35
1080	vw	1082	m			1076	w	"	13, 35
		1030	vw					$\delta(\text{OH})$	8-13
		850	sh			848	vs	$\nu(\text{CO}) + \nu(\text{CC}), (\text{COOH})$	14, 17, 23, 26
						806	vs	$\delta(\text{OCO}) + \nu(\text{CC})$	33, 35
						785	vw	"	19, 25, 26
745	vw	745	m			758	vs	$\delta(\text{OCO}) + \delta(\text{CH})$	17, 20, 33, 35
		706	sh			716	m	"	"
685	vw	688	vw			688	vw	$(\text{OCO}) + \text{ring def.}$	14, 20, 25-def, 33, 35-39
						673	m	"	"
644	vw	644	w			644	w	"	14, 20, 29
						578	w	"	14, 20, 32
						546	w	"	14

Table 4. Continued.

468	m,bd	485	s			$\nu(\text{FeO})$	51, 63-72
				434	s	$\rho_r(\text{CO}_2^-) +$ ring def.	21, 25-27
		425	m,bd			$\nu(\text{FeO})$	25, 51, 63-72
				403	s	$\rho_r(\text{OCO}) +$ ring, def.	21, 25-27
				333	m	$\rho_r(\text{OCO})$	20, 23, 25, 26, 33

<sup>a</sup> The intensity abbreviations are: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, bd = broad, sh = shoulder.

<sup>b</sup> The following abbreviations are used for the different vibrations:  $\nu$ (stretching),  $\nu_a$ (antisymmetric stretching),  $\nu_s$ (symmetric stretching),  $\delta$ (bending),  $\rho_r$ (rocking),  $\pi$ (out-of-plane bending), ring def. (ring deformation), (Ref. 27, p. 218).

Table 5. The wave numbers and assignments of the infrared absorption bands of the precipitated chromium(III) salts.

$\text{Cr}_3(\text{OH})_{12}(\text{O}_2\text{C})_2\text{C}_6\text{H}_4$ , (I)	Comments	$\text{Cr}(\text{OH})_3 \cdot 1.75\text{H}_2\text{O}$ , (III)	Comments	Assignment	Reference
3350	vs, bd	3350	vs, bd	$\nu(\text{CrOH}) + \nu(\text{HOH})$	45, 53, 70
2915	sh	2920	sh	$\nu(\text{OH})$	45, 53, 70
		1620	sh	$\delta(\text{HOH})$	53, 77
1600	sh			$\nu(\text{CO})$ or $\nu(\text{CC})$	17, 31, 32
1535	vs			$\nu_a(\text{CO}_2^-)$	23, 24, 29-32
1482	vw			$\nu(\text{CC})$	8, 16, 17, 34
		1458	m, bd	$\delta(\text{CrOH})$	51, 63-71
1440	sh			$\nu_s(\text{CO}) + \nu(\text{CC})$	17, 25-27
1400	vs			$\nu_s(\text{CO}_2^-) + \nu(\text{CC})$	17, 25-27, 33
		1380	sh	$\delta(\text{CrOH})$	51, 63-71
1290	sh			$\nu_s(\text{CO}) + \delta(\text{OCO})$	25, 27, 33
1260	sh			»	»
1142	vw			$\delta(\text{OH})$	13
1090	vw			$\delta(\text{OH})$	13
		825	w, bd	$\nu(\text{CrO})$	51, 63-71
747	w			$\delta(\text{OCO}) + \delta(\text{CH})$	17, 33
690	vw			$\delta(\text{OCO}) +$ ring def.	20, 25-27, 33, 36-39
650	vw			»	»
500	m, bd	507	s, bd	$\nu(\text{CrO})$	51, 63-71, 78

modes of the benzene ring,<sup>8,16,17,34</sup> and the strong band at 1377  $\text{cm}^{-1}$  from the symmetric CO stretching and CC stretching vibrations.<sup>25-27</sup> The band at 1278  $\text{cm}^{-1}$  is due to CO stretching and OCO deformation vibrations.<sup>25-27</sup> The very strong bands at 848  $\text{cm}^{-1}$  and 806  $\text{cm}^{-1}$  are not generally found in the spectra of the precipitated iron(III) and chromium(III) phthalates, but could obviously derive from the OCO stretching or deformation modes of the COOH group and the CC stretching vibrations of the benzene ring.<sup>17,33,35</sup>

Table 6. The wave numbers and assignments of the infrared absorption bands of the precipitated aluminium(III) salts.

$\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , (I) $\text{cm}^{-1}$	Comments	$\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , (III) $\text{cm}^{-1}$	Comments	Assignment	Reference
3420	vs, bd	3420	vs, bd	$\nu(\text{AlOH}) + \nu(\text{HOH})$	45, 53, 59-62, 81
2920	sh	2920	sh	$\nu(\text{OH})$	46-61
2415	w	2400	vw	$\nu(\text{OH})$	46-61
1762	vw	1762	w	$\nu(\text{OH})$	46-61
1620	m	1622	m	$\delta(\text{HOH})$	53, 55-58, 62, 81
1377	vs	1377	vs	$\delta(\text{AlOH})$	51, 63-71
915	w, bd	930	w, bd	$\delta(\text{AlOH})$	51, 59-71, 81
830	vw	830	vw	$\nu(\text{AlO})$	51, 62-71
570	s, bd	560	s, bd	$\nu(\text{AlO})$	25, 68, 72, 82
350	sh	350	sh	Vibration modes of lattice $\text{H}_2\text{O}$ or $\nu(\text{AlOH})$	59, 66-68, 82

In the spectral region  $800-250\text{ cm}^{-1}$ , the bands at  $758\text{ cm}^{-1}$  and  $716\text{ cm}^{-1}$ , which are observed as medium, weak, or absent in the spectra of the basic iron(III) and chromium(III) phthalates, are obviously also due to the OCO deformation vibrations of the unionized carboxylic group and the CH deformation vibrations of the benzene ring.<sup>17,33</sup> The medium or strong bands at  $673$ ,  $434$ ,  $403$ , and  $333\text{ cm}^{-1}$ , which are not observed in the spectra of the other phthalates investigated are possibly due to the OCO and ring deformation vibrations.<sup>25-27,36-39</sup>

*The iron(III) compounds.* It is to be noted that an iron precipitate was obtained with all three precipitation methods. With the first, a brown precipitate was formed, which was easily separable from the mother liquor (Table 1). After standing for a few days, the precipitate dissolved completely in the mother liquor, which became dark red-brown. When the second method was used, precipitation with  $0.5\text{ M}$  potassium biphthalate solution, an easily separable, pale-brown precipitate was obtained (Table 1). This did not dissolve upon standing in the mother liquor, which remained colourless for a longer time. The precipitation with sodium hydroxide (method III) gave a heavy, dark-brown product (Table 1).

It seems to be typical of the precipitations that in the first case (method I), a complicated basic iron oxide hydroxide phthalate and in the second case (method II), a basic iron hydroxy biphthalate are formed. These may be polymerized and have very complicated structures. In the third case (method III), the formation of ferric hydroxide is most probable.

Although performed in ethanolic ( $50$  or  $90\%$ ) water solutions, the heterometric studies by Bobtelsky and Bar-Gadda<sup>40</sup> of iron, chromium, and aluminium phthalate complexes and their mixtures indicate that individual metal phthalate complexes are also precipitated from the mixed solutions of the metals, either successively or simultaneously. This observation supports the accepted research method of analytical precipitation, although it does not exclude the possible formation of mixed basic metal phthalate complexes during the analytic procedure.<sup>1</sup>

It is interesting to note that Galwey,<sup>41</sup> following the observations of Bobtelsky and Bar-Gadda,<sup>40</sup> precipitated a pale brown product of the composition  $C_8H_5FeO_5 \cdot 0.5H_2O$  by adding ferric chloride (dissolved in 50 % ethanol-water) to a phthalic acid-ammonium hydroxide solution (50 % ethanol-water). This formula is very close to the composition of the precipitate obtained by method II in the present study (Table 2).

According to the literature quoted in Gmelin,<sup>42</sup> alkaline hydroxides precipitate from ferric salt solutions as hydrated ferric oxide gel having a varying water content. The thermogravimetric results (Fig. 1, Table 2) suggest that the precipitated ferric hydroxide with the procedure used in the present study, reaches the composition  $Fe_2O_3 \cdot 3H_2O$ , which corresponds to the hydroxide  $Fe(OH)_3$ . The later studies of Dey and Ghosh<sup>43</sup> on precipitations with sodium hydroxide from ferric chloride solutions support the present conclusions concerning the hydroxide precipitation.

The probable compositions and possible decomposition reactions derived from the thermogravimetric curves (Fig. 1, curves 2–4) and from the combustion analyses of the iron precipitates prepared by the three different precipitation methods (I, II, and III) are presented in Table 2. The temperature ranges of the reactions are compared with those of the DTA peaks (Fig. 2, curves 2–4) in Table 3.

In the thermal decomposition of the basic iron phthalate (Fig. 1, curve 2 and Table 2), an interesting plateau between 342° and 384°C can be seen. The suggested intermediate corresponding to this feature may be formulated<sup>44</sup> as  $Fe_2O_3 \cdot CO_2$ .

The DTA curves show an exothermic peak in the temperature range 400–500°C (Table 3) from the decompositions of all iron compounds. This is obviously connected with the formation of a stable product ( $Fe_2O_3$ ) from more reactive intermediates.

The IR spectra of the iron(III) compounds precipitated by the three different methods show a strong, broad band at 3700–3000  $cm^{-1}$  (Fig. 3, curves 2–4 and Table 4), which is strongest for the iron hydroxide biphthalate complex and weakest for iron(III) hydroxide. These bands are due to the OH stretching vibrations of the metal hydroxide groups.<sup>45–61</sup> From the intensity of the band, these stretching vibrations are especially unrestrained in the iron hydroxide biphthalate complex. To some extent, the bands may also be due to the OH stretching vibrations of lattice water.<sup>46–52</sup> Potassium biphthalate shows no band in this region.

The shoulders in the spectra at about 2900  $cm^{-1}$  are obviously also due to the OH stretching vibrations of metal hydroxide groupings or lattice water, depending on the composition of the compound. The medium band at 1700  $cm^{-1}$  in the spectrum of the iron(III) hydroxide biphthalate complex, confirms the presence of the unionized carboxylic group.<sup>8–15,19–28</sup>

The appearance or absence of a band at about 1620  $cm^{-1}$  in the spectra of metal hydroxides (due to the HOH bending modes of water) has been used to prove, respectively, the existence of water of the hydroxide form.<sup>53</sup> Using this criterion, the weakness of the band in the spectrum of the ferric compound precipitated with sodium hydroxide only (method III) shows that the

compound is better represented by the  $\text{Fe}(\text{OH})_3$  form than the  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , at least after treatment of the precipitate.<sup>55-58,62</sup>

The strong bands at 1530, 1400, 1380  $\text{cm}^{-1}$  and 1540, 1400  $\text{cm}^{-1}$ , respectively, in the spectra of the basic iron(III) phthalate and biphthalate, have the same designations as in potassium biphthalate. The medium bands at 1145 and 1082  $\text{cm}^{-1}$  in the spectrum of iron(III) biphthalate indicate an increase in the OH deformation vibrations compared to the other phthalates studied.

The medium band at 468  $\text{cm}^{-1}$  and the strong band at 485  $\text{cm}^{-1}$  in the spectra of the basic iron(III) phthalate and biphthalate, respectively, and which are not found for potassium biphthalate, should have their origin in the FeO stretching vibrations.<sup>63-71</sup>

The weak or medium broad bands at 1465, 1330 and 425  $\text{cm}^{-1}$  in the spectrum of iron(III) hydroxide are apparently also due to the FeOH bending and FeO stretching vibrations,<sup>63-71</sup> respectively.

The absence of bands <sup>46-51,62,72</sup> typical of  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  in the spectral range 800–250  $\text{cm}^{-1}$  in the spectrum of the precipitated iron(III) hydroxide confirms that it is not a question of a hydrated iron(III) oxide, but mainly of the iron(III) hydroxide. On the contrary the iron(III) phthalates show a medium or strong band at 460–490  $\text{cm}^{-1}$ , which appears as a strong band in the spectrum of  $\alpha\text{-Fe}_2\text{O}_3$  and as a weak band or shoulder for the other iron oxides. These observations indicate the iron oxide contents of the basic iron phthalates.

*The chromium(III) compounds.* By precipitation of chromium(III) ions according to the analytical scheme <sup>1</sup> (method I), a dark-green, easily separable precipitate was formed (Table 1). When allowed to stay several days in the mother liquor, it dissolved completely and the colourless solution became dark-green. No precipitate was formed when potassium biphthalate alone was used as the precipitating agent (method II), but the solution was coloured dark green (Table 1). With sodium hydroxide (method III), a green precipitate was formed (Table 1).

The precipitate formed by the method I has a very complicated composition and is obviously a polymer. It decomposes on heating in three stages, the probable processes for which are interpreted from the thermogram (Fig. 1, curve 5) and presented in Table 2. The results point to a partial sublimation of the product during the decomposition. The thermogravimetric temperature ranges are compared with the DTA peaks (Fig. 2, curve 5) in Table 3. The exothermic peak found (693°C) obviously corresponds to the formation of  $\text{Cr}_2\text{O}_3$ .

The thermogravimetric results (Fig. 1, curve 6 and Table 2) clearly show that the precipitate obtained with sodium hydroxide has, after the treatment described, a composition corresponding to a hydrated chromium(III) hydroxide. Its DTA curve (Fig. 2, curve 6) also shows an exothermic peak (Table 3) at 410°C (*cf.* the iron compound above), which again clearly corresponds to the formation of chromium(III) oxide.

The studies of Higashi *et al.*<sup>73</sup> on chromium(III) complexes with phthalic acid show the difficulties of precipitating a basic chromium(III) phthalate complex containing potassium. This is obviously still more difficult when sodium hydroxide is used to adjust the pH of the solution, as in the analytical

scheme<sup>1</sup> (method I). From the consistency of the present combustion analysis with respect to carbon and hydrogen and the thermogravimetric chromium residue, it follows that the alkali metal content of this precipitate is probably negligible or zero, as has been accepted.

In their heterometric experiments, Bobtelsky and Bar-Gadda<sup>40</sup> found that excess phthalate or chromium(III) ions dissolved the precipitate of chromium phthalate formed. It is therefore easily understood that no precipitate was obtained by using potassium biphthalate alone as the precipitating agent (method II).

On the basis of polarographic rate studies, Hamm *et al.*<sup>74</sup> have concluded that the rate determining step in the reaction process of carboxylic acids (among others the phthalate anion) with chromium(III) ions is the escape of a water molecule from the hexahydrated chromium(III) ion. Conversely, the slow uptake of water molecules by the chromium(III) ions in the basic chromium phthalate precipitate may explain its slow back-solubility into the mother liquor.

According to Franco and Sing,<sup>75</sup> no pronounced exothermic peak associated with a glow phenomenon has been observed in the DTA curve of the transformation of  $\text{CrO}_2$  to  $\alpha\text{-Cr}_2\text{O}_3$ . However, since both DTA curves of the present chromium precipitates show an exothermic peak, it is evident that although the precipitates could to some extent contain  $\text{CrO}_2$  as an intermediate during the decomposition processes, they should nevertheless leave chromium(III) oxide as the decomposition end-product,<sup>76</sup> as is accepted in Table 2.

Both the precipitated chromium(III) compounds show a very strong and broad band at  $3350\text{ cm}^{-1}$  and weak shoulders at about  $2915\text{--}2920\text{ cm}^{-1}$  (Fig. 3, curves 5 and 6, and Table 5). These are due to the OH stretching vibrations of the CrOH groupings<sup>45,53,70</sup> and lattice water.

The almost complete absence of the band at  $1620\text{ cm}^{-1}$  due to the HOH bending vibrations in the spectrum of the chromium hydroxide precipitate confirms the product to be almost wholly in the  $\text{Cr}(\text{OH})_3$  form.<sup>53,77</sup>

The strong bands at  $1535$  and  $1400\text{ cm}^{-1}$  in the spectrum of the basic chromium(III) phthalate complex should have the same origin as those of potassium biphthalate in the same region. The medium, broad band at  $500\text{ cm}^{-1}$  supposedly arises from the CrO stretching modes.<sup>51,63-71</sup>

The medium and strong bands at  $1458$  and  $507\text{ cm}^{-1}$  in the spectrum of  $\text{Cr}(\text{OH})_3$  are due to the CrOH bending and CrO stretching vibrations,<sup>51,63-71</sup> respectively. The complete lack of the bands in the region  $800\text{--}250\text{ cm}^{-1}$ , typical of chromium(III) oxide,<sup>51,78</sup> shows the precipitate to consist rather of the hydroxide form than of a hydrated oxide.

*The aluminium(III) compounds.* Aluminium(III) ion was precipitated as white amorphous products both according to the analytical scheme<sup>1</sup> (method I) and with sodium hydroxide solution (method III), but not when precipitating with potassium biphthalate alone when no changes were observed in the clear solution (Table 1).

The thermogravimetric analyses showed that the products precipitated both by method I (Fig. 1, curve 7 and Table 2) and by method III (Fig. 1, curve 8 and Table 2) were aluminium oxide hydrates, the former containing five and the latter six water molecules. The proposed dehydration processes

for both hydrates are presented in Table 2. These and their temperature limits are compared with the DTA peaks (Fig. 2, curves 7 and 8) of the products in Table 3. In contrast to the iron and chromium compounds discussed above, the DTA curves do not show any exothermic processes. This confirms the opinion that the precipitates are already in the hydrated aluminium oxide forms at the beginning of the thermal processes.

For general views on the dehydration processes of precipitated aluminium hydroxides or oxide hydrates the reader is referred to Gmelin.<sup>79</sup>

The potentiometric studies on the complexing of aluminium ions with phthalate ions performed by Napoli and Liberti<sup>80</sup> support the nonprecipitation of aluminium phthalate complexes observed here. They found two successive soluble aluminium phthalate complexes, the stability constants of which were determined.

The precipitated aluminium compounds also exhibit both a strong, broad band at  $3420\text{ cm}^{-1}$  and a weak shoulder at  $2920\text{ cm}^{-1}$  (Fig. 3, curves 7 and 8, and Table 6), which are due to the OH stretching vibrations of the aluminium hydroxyl groupings<sup>46,53</sup> and the lattice water. Two weak bands are seen in both spectra at  $2400\text{--}2415\text{ cm}^{-1}$  and  $1762\text{ cm}^{-1}$ , obviously corresponding to the OH stretching vibrations of the AlOH groupings and the lattice water.<sup>46,61</sup>

It can be seen from the spectra in Fig. 3 and Tables 4–6 that the frequency of the OH stretching mode of the MOH grouping in the region  $3700\text{--}3000\text{ cm}^{-1}$  increases in the series  $\text{Cr(III)} < \text{Fe(III)} < \text{Al(III)}$ . The OH bond is obviously shortened, the bond strength increased and the hydrogen bond  $\text{O}\cdots\text{H}\cdots\text{O}$  formation decreased in this series.<sup>27,53</sup>

The medium HOH bending bands at  $1620\text{ cm}^{-1}$  in the spectra of both aluminium precipitates show the compositions to be closer to the oxide hydrates than to the hydroxides.<sup>53,55–58,62,61</sup>

Both aluminium compounds show strong bands at  $1377\text{ cm}^{-1}$  and  $570\text{--}560\text{ cm}^{-1}$ , contributed by the AlOH bending<sup>51,63–71</sup> and AlO vibrations,<sup>72,82</sup> respectively. This latter band is also found in the spectrum of  $\alpha\text{-Al}_2\text{O}_3$ <sup>51,66–68,82</sup> which further indicates that we are dealing more with hydrated aluminium oxides than with hydroxides.

## SUMMARY

The main conclusions of the present study may be summarized as follows:

1. For simplicity, the iron, chromium, and aluminium precipitates obtained by the analytical procedure (method I) were presented in the analytical scheme<sup>1</sup> in the forms  $[\text{Fe}(\text{OH})\text{Ph}]_n$ ,  $[\text{Cr}(\text{OH})\text{Ph}]_n$ , and  $\text{Al}(\text{OH})_3$ . These ought now be considered in the light of this study.

2. The iron(III) and chromium(III) ions are most probably precipitated in the analytical scheme<sup>1</sup> as polymerized hydroxy phthalates, whereas the aluminium(III) ions are precipitated as hydrated aluminium(III) oxides.

3. The micro combustion analyses and thermogravimetric results of the basic iron(III) and chromium(III) phthalates studied are parallel, and confirm the conclusions about the compositions.

4. The DTA curves show considerably more structural and composition changes than would generally be concluded from the TG curves. The DTA

curves of iron(III) and chromium(III) compounds show an exothermic peak in the temperature range 400°–700°C, which indicates the formation of the oxides  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ .

5. The infrared spectra confirm the conclusions drawn concerning the compositions of the compounds studied.

#### REFERENCES

1. Lumme, P. and Tummaavuori, J. *Acta Chem. Scand.* **27** (1973) 851.
2. *Stability Constants of Metal-ion Complexes*, Spec. Publ. No. 17, The Chem. Soc., London 1964; *Stability Constants of Metal-ion Complexes*, Suppl. No. 1, Spec. Publ. No. 25, The Chem. Soc., London, 1971.
3. Newkirk, A. E. and Laware, R. *Talanta* **9** (1962) 169.
4. Belcher, R., Erdey, L., Paulik, F. and Liptay, G. *Talanta* **5** (1960) 53.
5. Duval, C. and Wadier, C. *Anal. Chim. Acta* **23** (1960) 541.
6. Duval, C. *Anal. Chim. Acta* **13** (1955) 32.
7. Caley, E. R. and Brundin, R. H. *Anal. Chem.* **25** (1953) 142.
8. Flett, M. St. C. *Characteristic Frequencies of Chemical Groups in the Infra-red*, Elsevier, London 1963, pp. 34–35.
9. Hadzi, D. and Sheppard, N. *Proc. Roy. Soc. London A* **216** (1953) 247.
10. Flett, M. St. C. *J. Chem. Soc.* **1951** 962.
11. Flett, M. St. C. *Spectrochim. Acta* **18** (1962) 1537.
12. Lusi, H. *Anal. Chem.* **31** (1959) 910.
13. Colthup, N. B., Daly, L. H. and Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*, Academic, London 1964, pp. 257–262.
14. Bentley, F. F., Ryan, M. T. and Katon, J. E. *Spectrochim. Acta* **20** (1964) 685.
15. Bentley, F. F., Smithson, L. D. and Rozek, A. L. *Infrared Spectra and Characteristic Frequencies* ~ 700–300  $\text{cm}^{-1}$ , Interscience, London 1968, pp. 136, 137, 150 and 151.
16. Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, Methuen, London 1958, p. 90.
17. Ref. 13, pp. 220–230.
18. Whiffen, D. H. *Spectrochim. Acta* **7** (1955) 253.
19. Schmelz, M. J., Nakagawa, I., Mizushima, S. and Quagliano, J. V. *J. Am. Chem. Soc.* **81** (1959) 287.
20. Itoh, K. and Bernstein, H. J. *Can. J. Chem.* **34** (1956) 170.
21. Green, J. H. S., Kynaston, W. and Lindsey, A. S. *Spectrochim. Acta* **17** (1961) 486.
22. Vrátný, F., Rao, C. N. R. and Dilling, M. *Anal. Chem.* **33** (1961) 1455.
23. Hester, R. E. and Plane, R. A. *Inorg. Chem.* **3** (1964) 513.
24. Nakamoto, K., Morimoto, Y. and Martell, A. E. *J. Am. Chem. Soc.* **83** (1961) 4528.
25. Fujita, J., Martell, A. E. and Nakamoto, K. *J. Chem. Phys.* **36** (1962) 324, 331.
26. Schmelz, M. J., Miyazawa, T., Mizushima, S., Lane, T. J. and Quagliano, J. V. *Spectrochim. Acta* **9** (1957) 51.
27. Nakamoto, K. and McCarthy, P. J. *Spectroscopy and Structure of Metal Chelate Compounds*, Wiley, London 1968, pp. 270–273.
28. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Ed., Wiley-Interscience, London 1970, pp. 244–246.
29. Wilmhurst, J. K. *J. Chem. Phys.* **23** (1955) 2463.
30. Ref. 27, p. 269.
31. Condrate, R. A. and Nakamoto, K. *J. Chem. Phys.* **42** (1965) 2590.
32. Tsuboi, M., Onishi, T., Nakagawa, I., Shimanouchi, T. and Mizushima, S. *Spectrochim. Acta* **12** (1958) 253.
33. Ref. 28, pp. 222–223, 232–243.
34. Wexler, A. S. *Spectrochim. Acta A* **23** (1967) 1319.
35. Lumme, P. *Suomen Kemistilehti B* **31** (1958) 294; **B 30** (1957) 204.
36. Bentley, F. F. and Wolfarth, E. F. *Spectrochim. Acta* **15** (1959) 165.
37. Ref. 13, p. 342.
38. Jones, L. A. and McLaren, E. *J. Chem. Phys.* **22** (1954) 1796.



39. Ref. 15, pp. 45, 69.
40. Bobtelsky, M. and Bar-Gadda, I. *Anal. Chim. Acta* **9** (1953) 446.
41. Galwey, A. K. *J. Chem. Soc.* **1965** 4235.
42. *Gmelins Handbuch der anorg. Chemie*, 8 Aufl., Eisen, Syst. Nr. 59, Teil B, Liefer. 1, Verlag Chemie, Weinheim 1930, pp. 26, 34, 36, 63, 122–131, 134.
43. Dey, A. K. and Ghosh, S. *J. Ind. Chem. Soc.* **27** (1950) 65.
44. Ref. 42, Liefer. 2, pp. 508, 509, 512.
45. Busing, W. R. and Morgan, H. W. *J. Chem. Phys.* **28** (1958) 998.
46. Lucchesi, P. J. and Glasson, W. A. *J. Am. Chem. Soc.* **78** (1956) 1347.
47. Brink, G. *Spectrochim. Acta* **A 28** (1972) 1151.
48. Miller, F. A. and Wilkins, C. H. *Anal. Chem.* **24** (1952) 1253.
49. Hunt, J. M., Wisherd, M. P. and Bonham, L. C. *Anal. Chem.* **22** (1950) 1478.
50. Brame, E. G., Jr., Margrave, J. L. and Meloche, V. W. *J. Inorg. Nucl. Chem.* **5** (1957) 48.
51. McDevitt, N. T. and Baun, W. L. *Spectrochim. Acta* **20** (1964) 799.
52. Ref. 28, pp. 166, 167.
53. Siebert, H. *Anwendungen der Schwingungsspektroskopie in der anorganischen Chemie*, Springer-Verlag, Berlin 1966, pp. 90–92 and 145.
54. Glemser, O. *Angew. Chem.* **73** (1961) 785.
55. Glemser, O. and Rieck, G. *Z. anorg. allgem. Chem.* **297** (1958) 175.
56. Cannon, C. G. *Spectrochim. Acta* **10** (1958) 341.
57. Maurin, M. *Bull. Soc. Chim. France* **1962** 1497.
58. Schwarzmann, E. *Z. anorg. allgem. Chem.* **317** (1962) 176.
59. Frederickson, L. D., Jr. *Anal. Chem.* **26** (1954) 1883.
60. Glemser, O. and Hartert, E. *Z. anorg. allgem. Chem.* **283** (1956) 111.
61. Braunscholtz, J. T., Hall, G. E., Mann, F. G. and Sheppard, N. *J. Chem. Soc.* **1959** 868.
62. Hartert, E. and Glemser, O. *Z. Elektrochem.* **60** (1956) 746.
63. Glemser, O. *Nature* **183** (1959) 1476.
64. Glemser, O. and Hartert, E. *Naturwiss.* **40** (1953) 552.
65. Dupuis, T. *Rec. Trav. Chim.* **79** (1960) 518.
66. Van der Elsken, J. and Robinson, D. W. *Spectrochim. Acta* **17** (1961) 1249.
67. Gamo, I. *Bull. Chem. Soc. Japan* **34** (1961) 760, 765, 1430, 1433.
68. Nakagawa, I. and Shimanouchi, T. *Spectrochim. Acta* **20** (1964) 429.
69. Scargill, D. *J. Chem. Soc.* **1961** 4444.
70. Ferraro, J. R., Driver, R., Walker, W. R. and Wozniak, W. *Inorg. Chem.* **6** (1967) 1586.
71. Hewkin, D. J. and Griffith, W. P. *J. Chem. Soc. A* **1966** 472.
72. Ref. 15, the spectra Nos. 1528–1530.
73. Higashi, K., Hori, K. and Tsuchiya, R. *Bull. Chem. Soc. Japan* **40** (1967) 2569.
74. Hamm, R. E., Johnson, R. L., Perkins, R. H. and Davis, R. E. *J. Am. Chem. Soc.* **80** (1958) 4469.
75. Franco, M. A. A. and Sing, K. S. W. *J. Thermal Anal.* **4** (1972) 47.
76. *Gmelins Handbuch der anorg. Chemie*, 8 Aufl., Chrom, Syst. Nr. 52, Teil B, Verlag Chemie, Weinheim 1962, pp. 8, 9, 11, 13–15, 26–29, 42, 59–60, 64–66, 71–74, 80–81, 90, 95, 99, 100, 103, 105, 107, 113.
77. Benoit, A. *Spectrochim. Acta* **19** (1963) 2011.
78. Ref. 15, the spectrum No. 1515.
79. *Gmelins Handbuch der anorg. Chemie*, 8 Aufl., Aluminium, Syst. Nr. 35, Teil B, Liefer. 1, Verlag Chemie, Weinheim 1933, pp. 102, 107, 114.
80. Napoli, A. and Liberti, A. *Gazz. Chim. Ital.* **100** (1970) 906.
81. Ginsberg, H., Hüttig, W. and Stiehl, H. *Z. anorg. allgem. Chem.* **309** (1961) 233; **318** (1962) 238.
82. Ref. 15, the spectrum No. 1507.

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