Journal of Thermal Analysis, Vol. 36 (1990) 2365-2373

THE THERMAL DECOMPOSITION OF SOME Cr(III) COMPLEXES

M. Grotowska, R. Wojciechowska and *W. Wojciechowski*

INSTITUTE OF INORGANIC CHEMISTRY AND METALLURGY OF RARE ELEMENTS,
POLYTECHNICAL UNIVERSITY OF WROCLAW, 50-370 WROCLAW, POLAND

(Received October 3, 1988; in revised form August 3, 1990)

The thermal decomposition reactions of the following chromium(III) complexes were investigated: $Cr(CH_3COO)_3 \cdot 2\,H_2O$, $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 2\,H_2O$ and $[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl \cdot 6\,H_2O$. Simultaneous TG/DTG/DTA were applied non-isothermal conditions. From the recorded curves, the activation energies E_a were calculated for all the thermal decomposition steps. Appropriate chemical reactions were attributed to the thermal effects, with consideration to the X-ray diffraction and IR spectra results.

The coordination compounds are subject to ever increasing research by derivatography because of the various molecular structures of these compounds and the great variety of ligands and central ions, and also because of the role played by coordination compounds and their high-temperature decomposition products in catalytic processes. Application of derivatography may also provide qualitative information regarding the stability of the crystal lattice, the character of the bonding in the molecules, the mechanism of their decomposition and the kinetics of these reactions. Obviously, this research must be related with the results of other structural investigations, e.g. X-ray crystallography or spectroscopy. This work presents the results of such studies on the following compounds:

$$Cr(CH_3COO)_3 \cdot 2\,H_2O,$$

$$[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl \cdot 2\,H_2O$$

and

$$[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6\,H_2O.$$

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

In the first of these compounds, the chromium coordination sphere exhibits distorted octahedral symmetry [1]. The two remaining complexes are trinuclear compounds in which three chromium ions form an equilateral triangle, with the oxygen ion at the centre of the triangle [1]. The nearest coordination sphere of each chromium(III) ion again exhibits distorted octahedral symmetry. The studies on these compounds had the aim of obtaining information on the influence of the molecular structure on the mechanism of decomposition and the magnitude of the apparent activation energy.

Experimental and discussion

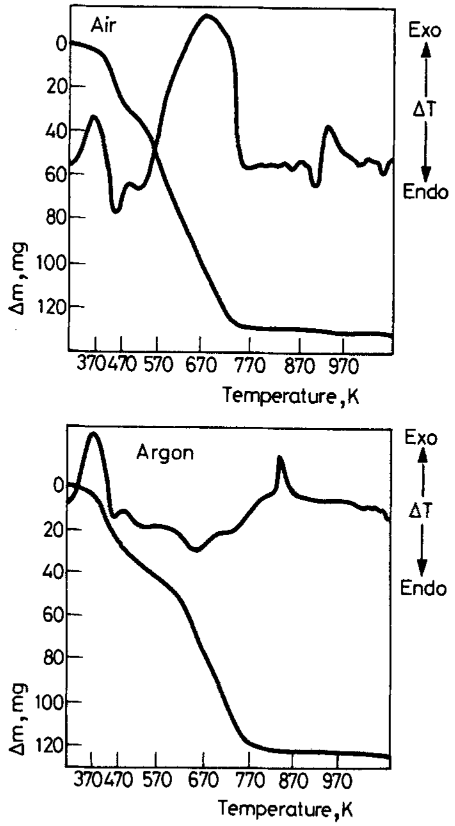

Fig. 1 DTA and TG curves of $Cr(CH_3COO)_3 \cdot 2H_2O$

Thermoanalytical measurements were performed under nonisothermal conditions on a Paulik-Paulik-Erdey 3427 T derivatograph in an atmosphere of air or nitrogen in the temperature range 293-1073 K. The X-ray measurements were carried out on a DRON 2 diffractometer with CuK_α radiation. The infrared spectra were measured on Perkin-Elmer 176 and Spekord 70 spectrophotometers in KBr matrices. X-ray and spectroscopic measurements were performed on samples annealed at temperatures determined from the DTA and TG curves. The results are presented in Figs 1-3 and Tables 1-3.

It is interesting to note that $[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl\cdot 2H_2O$ undergoes a constant mass loss in the second stage of decomposition in air atmosphere. This mass loss is caused by the presence of CrO_3 (Table 1), which sublimes and undergoes decomposition [2].

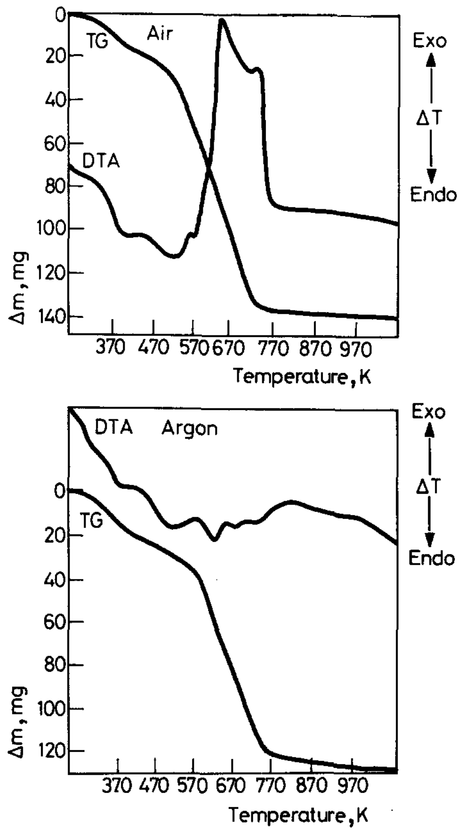

Fig. 2 DTA and TG curves of $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 2H_2O$

Table 1 Results of thermal analysis of Cr (III) complexes in air and argon atmospheres

Compound	Stage	Range of temp., K	Weight loss, %		Composition of residue	Atmosphere
			Theor.	Obser.		
$Cr(CH_3COO)_3 \cdot 2H_2O$	I	338-478	13.6	13.8	$Cr(CH_3COO)_3$ (s), H_2O (g)	
	II	478-740	58.0	57.5	Cr_2O_3 (s), CO_2 (g), H_2O (g)	air
	III	888-1004	-	-	C_2O_3 (s)	
	I	353-480	13.6	13.2	$Cr(CH_3COO)_3$ (s), H_2O (g)	
	II	598-781	45.5	46.0	$Cr_2O_3 \cdot xCO_2$ (s) [14], C (s), CO (g), H_2O (g)	argon
	III	781-883	2.1	2.0	Cr_2O_3 (s), CO_2 (g)	
$[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 2H_2O$	I	313-608	33.7	33.0	$Cr_2O_3 \cdot xCO_2$ (s), CO_2 (g), H_2O (g), HCl (g)	
	II	608-748	38.0	37.0	Cr_2O_3 (s), CO_2 (g)	air
	I	318-568	18.0	18.0	$Cr(CH_3COO)_3$ (s), Cr_2O_3 (s), H_2O (g), HCl (g)	
	II	568-791	42.5	44.0	Cr_2O_3 (s), H_2O (g), CO (g), H_2 (g)	argon
$[Cr_3O(CH_2ClCOO)_3(H_2O)_3]Cl \cdot 6H_2O$	I	333-523	12.3	11.0	$[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl$ (s), H_2O (g)	air
	II	543-743		81.5	Cr_2O_3 (s), CrO_3, CO_2 (g), H_2O (g), HCl (g)	
	III	823-918			Cr_2O_3 (s)	
	I	458-563	12.3	11.0	$[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl$ (s), H_2O (g)	argon
	II	563-698	58.7	60.0	Cr_2O_3 (s), CO_2 (g), H_2O (g), CrO_3	
	III	698-708			Cr_2O_3 (s)	

Table 2 X-ray diffraction data of products of thermal decomposition of compounds: $Cr(CH_3COO)_3\cdot 2H_2O$ (I), $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 2H_2O$ (II), $[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl\cdot 6H_2O$ (III) compared with CrO_3 and Cr_2O_3

d Å		Compound I		Compound II		Compound II	
CrO_3	Cr_2O_3	740 K	910 K	600 K	750 K	570 K	700 K
1.43	1.43	1.42	1.42	1.42	1.42		1.42
					1.45		1.45
1.47	1.46			1.46	1.46		
1.56	1.58			1.64	1.57		
1.60				1.66			
1.68	1.67			1.68	1.67		1.66
1.71				1.72			
	1.81			1.81	1.80		
1.84			1.83	1.84	1.84		1.84
							1.88
1.96			2.00				
2.00	2.03		2.08				
	2.17			2.17	2.17		2.17
2.25				2.26			
2.36		2.30	2.31				
		2.43	2.42	2.40			
	2.47			2.47	2.50		2.47
	2.67		2.67	2.66	2.66		2.65
			2.74	2.74	2.74		
		2.81	2.82				
2.86		2.89	2.89				
			2.99	2.96	2.95		2.96
							3.01
3.40							
	3.62			3.70	3.65		3.63
		3.84					
				4.06	4.04		
4.20			4.24				

The results in Tables 2 and 3 confirm the data obtained from the thermoanalytical curves and contained in Table 1. Table 3 includes the positions of the absorption bands for $Cr_2O_3\cdot H_2O$, because the infrared spectral measurements were carried out at room temperature in a KBr matrix, which is hygroscopic.

The data from the DTA and TG curves may be used to calculate the kinetic parameters of the decomposition. There are several methods for this purpose, which differ in the manner of thermogravimetric curve approximation (e.g. the Redfern [5], Freeman-Carroll [6] and Fuosse [7] methods). We used the Coates-Redfern method, which usually leads to results in good agreement with those obtained with the Freeman-Carroll and Fuosse methods [8, 9].

The background of the method is the approximation of the exponential integral in the thermogravimetric curve equation by be expression in the form [10]:

$$\log\frac{g(\alpha)}{T^2}=\log\frac{ZR}{qE}\left(1-\frac{2RT}{E}\right)-\frac{E}{2.3RT}$$

where:
E is the activation energy, Z is the preexponential factor in the Arrhenius equation, $q=\frac{\mathrm{d}T}{\mathrm{d}t}$ and α is the measure of the conversion.

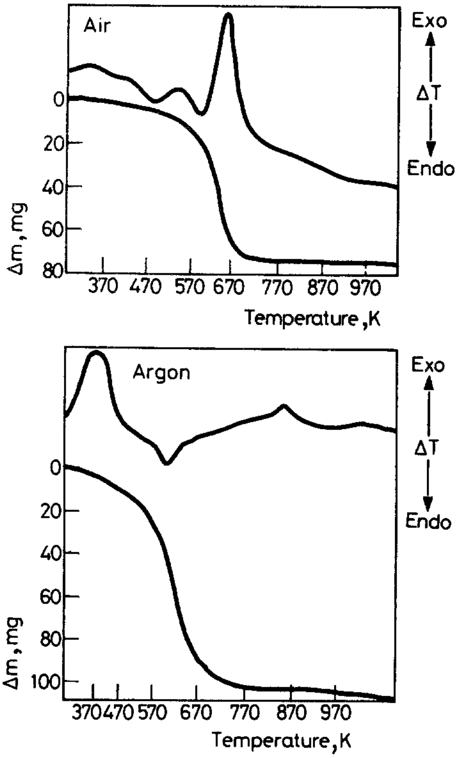

Fig. 3 DTA and TG curves of $[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl\cdot 6H_2O$

Table 3 Positions of absorption band IR spectra of compounds: $Cr(CH_3COO)_3 \cdot 2H_2O$ (I), $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 2H_2O$ (II), $Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl \cdot 6H_2O$ (III) compared with Cr_2O_3

$Cr_2O_3 \cdot H_2O$	Compound I		Compound II		Compound III		
	740 K	910 K	600 K	750 K	570 K		700 K
	390	390	410	410		amorphous compound	400
470							
550	570	570	575	575	545		570
630	665	665	630	630			630
790							
	850						
870	865	880					
1050	1030	1060	960	960			
1630	1665	1680	1630	1630	1610		1630
3100		3180					
	3300						
3400			3400	3400	3400		3400

In the version used here, the straight line $\log\frac{g(\alpha)}{T^2}$ *vs.* $1/T$ is obtained by the application of the least-square method. Calculations were performed by changing the n value: the appropriate n value is indicated by the maximum in the Jaffe correlation coefficient [11]. For the calculations reported in this paper, the code of Zsako [10] was used. The results are presented in Table 4.

The data obtained reveal that there are no significant differences between the mechanisms of decomposition of the mononuclear and trinuclear compounds (Table 1). In this case the formation of polynuclear clusters was considered. This indicates that the bonding in the Cr_3O^{n+} centre is weak. This is in agreement with the results of spectroscopic and magnetic investigations [12, 13]. From a comparison of the decomposition products formed in the individual stages of decomposition of the trinuclear compounds (Table 1), it is evident that the stability of the Cr_3O^{n+} centre depends on the remaining ligands. Such an explicit dependence could not be established from studies of the electronic spectra of these compounds.

Table 4 Kinetical parameters for thermal decomposition reaction in air and argon atmospheres

Compound	Air					Argon				
	Stage	E, kJ/mol	n	z	R	Stage	E, kJ/mol	n	z	R
Compound I	I	47.35	1.125	3.017	0.969	I	37.90	0.968	1.784	0.956
	II	58.43	1.609	1.828	0.989	II	118.65	2.547	6.567	0.991
	III	180.12	1.359	7.089	0.989	III	471.25	2.297	26.669	0.979
Compound II	I	9.89	0.218	–2.509	0.947	I	18.32	2.281	–0.529	0.949
	II	124.29	1.937	6.968	0.997	II	79.73	1.875	3.342	0.994
Compound III	I	38.87	0.953	1.426	0.995	I	36.19	0.891	0.737	0.988
	II	213.33	5.047	16.135	0.993	II	209.85	3.516	15.313	0.996
	III	250.02	1.641	12.356	0.991					

Compound I – $Cr(CH_3COO)_3 \cdot 2H_2O$
Compound II – $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 2H_2O$
Compound III –$[Cr_3O(CH_2ClCOO)_6(H_2O)_3]Cl \cdot 6H_2O$

References

1 S. C. Chang and G. A. Jeffrey, Acta Cryst., B26 (1970) 673.
2 A. F. Wells, Structural Inorganic Chemistry, Clarendon Press–Oxford, 1975, p. 946.
3 L. J. Mirkin, Spravocnik po rentgenostrukturnomu analizu polikristallow, Moskwa, 1961.
4 Atlas der Kunststoff-Analyse, Humel/Scholl, Vol. 2, Offenburg, 1973.
5 A. W. Coats and J. P. Redfern, Nature, 210 (1968) 68.
6 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
7 R. M. Fuoss, J. D. Salyer and H. S. Wilson, J. Polym. Sci., A2 (1964) 3147.
8 J. Sęstak, V. Satova and W. W. Wendlandt, Thermochim. Acta, 7 (1973) 447.
9 P. V. Khandikar, J. Thermal Anal., 93 (1987) 737.
10 J. Zsako and J. Zsako jr., J. Thermal Anal., 19 (1980) 333.
11 H. H. Jaffe, Chemical Rev., 53 (1953) 191.
12 M. Makles-Grotowska and W. Wojciechowski, Bull. Acad. Polon. Sci. Chim., 1 (1979) 59.
13 M. Makles-Grotowska and W. Wojciechowski, Bull. Acad. Polon. Sci. Chim., 1 (1979) 69.
14 V. W. Meloche and G. E. Kalbus, J. Inorg. Nucl. Chem., 6 (1958) 104.

Zusammenfassung — Für die Untersuchung der thermischen Zersetzungsreaktion der Chrom(III)-Komplexe $Cr(CH_3COO)_3 \cdot 2H_2O$ $[Cr_3O(CH_3COO)_6 \cdot (H_2O)_3]Cl2H_2O$ und $[Cr_3O(CH_2ClCOO)_6 \cdot (H_2O)_3]Cl6H_2O$ wurde simultane TG/DTG/DTA unter nichtisothermen Bedingungen eingesetzt. Ausgehend von den aufgezeichneten Kurven wurden für alle Schritte der Zersetzungsreaktion die E_a-Werte berechnet. In Übereinstimmung mit röntgenographischen und IR-spektroskopischen Ergebnissen wurden den thermischen Effekten passende chemische Reaktionen zugeordnet.