

## THERMAL INVESTIGATIONS OF SOME CHROMIUM(IV) COMPLEXES

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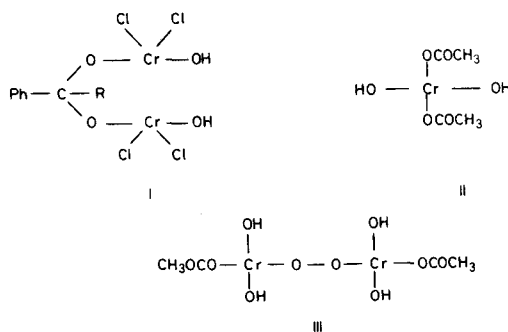
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The thermal decompositions of 15 solid products of reactions of chromyl chloride and chromyl acetate with alkylaromatics were studied by means of a derivatograph in argon and air atmospheres. In the case of the chromyl chloride complexes,  $2\text{Cr}^{\text{IV}}\text{O}_2\text{Cl}_2 \cdot \text{HR}$  (HR = hydrocarbon molecule), the formation of  $\text{Cr}_2\text{O}_3\text{Cl}_2$  was observed as a labile intermediate in the inert atmosphere, while in air the abrupt decomposition of the complexes leads to  $\text{Cr}_2\text{O}_3$  as a residue. The decompositions of monochromium(IV) hydroxoacetate and dichromium(IV) hydroxoacetate proceed through the intermediate  $\text{Cr}_2\text{O}_3(\text{CO}_3)$  both in argon and in air atmospheres. Characteristic temperatures are discussed and the activation energies  $E_a$  of the particular steps of thermal decompositions were calculated in all cases.

The thermal properties of compounds may provide useful information on the physicochemical properties. Moreover, the properties of almost any type of substance can be investigated by thermogravimetric analysis techniques. For this type of investigations, among other, numerous groups of metal chelates, mainly chelates of *d*- and *f*-elements, have been used [1-6]. A complex thermal study may yield information on the stages of chemical processes in a complex system.

The physicochemical properties of some chromium(IV) complexes have been the subject of our investigations for several years [7-9]. Whereas, a large number of studies have been devoted to the thermal analysis of chromium(III) and chromium(VI) compounds [4-6], there are virtually no reports concerning the thermal behaviour of chromium(IV) compounds.

In this paper, 15 chromium(IV)-containing solid products of the reactions of chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , and chromyl acetate,  $\text{CrO}_2(\text{CH}_3\text{COO})_2$ , with alkylaromatics have been investigated by thermal analysis. Chromyl chloride reacts with alkylaromatics such as toluene, ethylbenzene, *n*-propyl- and isopropylbenzene, diphenyl- and triphenylmethane to yield compounds  $2\text{CrO}_2\text{Cl}_2 \cdot \text{HR}$  (I) (HR = alkylaromatic), while with the same hydrocarbons chromyl acetate forms monochromium(IV) hydroxoacetate,  $\text{Cr}(\text{OH})_2(\text{CH}_3\text{COO})_2$  (II), or dichromium(IV) hydroxoacetate,  $\text{Cr}_2\text{O}_2(\text{OH})_4(\text{CH}_3\text{COO})_2$  (III), depending on the method of preparation [7, 8], but containing no hydrocarbon molecule.



All these compounds were studied magnetochemically, as well as by IR and UV-VIS spectroscopy [7–9].

The thermal decompositions of some pure hydrocarbons and of the metal salts of monocarboxylic acids have been carried out by several workers [10–15]. It is well known that the pyrolysis of metal salts of simple aliphatic acids leads to symmetrical aliphatic ketones. However, it appears from the pyrolysis that various compounds, simple or complex, are generated besides the main decomposition products. No data concerning the thermal decomposition of metal complexes with alkylaromatics are available in the literature. The present paper described for the first time the thermal decomposition processes of the above chromium(IV) complexes in inert and air atmospheres.

## Experimental

All the compounds studied were synthesized by the method described in [8].

Simultaneous TG/DTG/DTA curves were obtained with a Paulik–Paulik–Erdey OD-102 thermobalance, in air and argon atmosphere. The sample weight was maintained as nearly constant as possible (approximately 100 mg). The thermal curves were obtained using a programmed heating rate of 5 deg/min, and were observed in the temperature range of 293–1073 K. The thermal decomposition products corresponding to the discrete TG plateau regions were isolated. The starting compounds and the final products were characterized via the methods of elemental analysis.

The activation energies of the particular steps of decompositions of the compounds studied were calculated from the Kissinger [16] equation:

$$\frac{E_a \Phi}{RT_m^2} = k \cdot e^{-E_a/RT_m}$$

where  $E_a$  is the activation energy,  $\Phi = dT/dt$ ,  $T_m$  is the DTA peak temperature, and  $k$  is a coefficient. This was simplified by Piloyan et al. [17] as follows

$$\ln \Delta T = C - \frac{E_a}{RT}$$

where  $C$  is a constant.

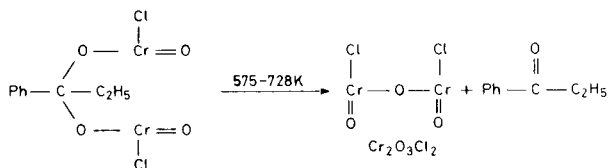
All the calculated values, together with the formulas of the complexes studied, are collected in Tables 1–3.

## Results and discussion

In the following discussion the results relating to the thermal behaviour (weight loss percentages, decomposition temperatures) and the activation energies of the particular steps of decompositions of a total of 15 chromium(IV) compounds in inert and air atmospheres are given.

### *Chromyl chloride reaction products*

Representative TG/DTA curves for the chromyl chloride–*n*-propylbenzene reaction product in argon and air atmospheres are presented in Fig. 1. Upon heating in argon atmosphere, chromyl chloride complexes lose two molecules of HCl in two steps. The DTA curve displays two exotherms, with  $T_m = 338$  and 387 K, respectively (see Table 1). The theoretical weight loss of each HCl molecule is 8.48%, but the TG curve shows 17.35% instead of the 16.96% expected for the two steps. This is obviously due to the later decomposition of the involved molecules, and all the decomposition products have not left before the beginning of evolution of the ketone molecule in the following reaction:



Freeman and his coworkers [18, 19] have demonstrated that if the chromyl chloride–alkane adduct is not isolated, but decomposed under reductive hydrolytic conditions, good to excellent yields of aldehydes and ketones are obtained. The DTA curve shows the process to be endothermic in the temperature range 575–728 K. The theoretical level of  $\text{Cr}_2\text{O}_3$  is 35.37%, whereas the content found from the TG curve is 51.53% at 750 K. This is due to the  $\text{Cr}_2^{\text{IV}}\text{O}_3\text{Cl}_2$  molecule, which is stable up to 873 K (the theoretical value of its content is 51.87%, and the sharp exotherm with  $T_m = 880$  K shows its decomposition to  $\text{Cr}_2\text{O}_3$  and  $\text{Cl}_2$ ).

The general features of the thermal decompositions of all the chromyl chloride products in dynamic air atmosphere are seen to be very similar. The decomposition of  $2 \text{Cr}^{\text{IV}}\text{O}_2\text{Cl}_2 \cdot \text{HR}$  molecules is not a single process, but consists of the superposition of several exothermic processes, indicated by two regions of overlapping exo-

Table 1 Results of thermal analysis of chromyl chloride complexes in argon and air atmospheres

Compound	Range of temp., K	DTA peak temp., K	Activation energy, kJ/mol	Weight loss, %		Composition of residue	Atmosphere
				Observed	Theoretical		
1. $2 \text{CrIV} \text{O}_2 \text{Cl}_2 \cdot \text{T}$ (T = toluene)	303-370	348	53	9.00	9.07		
	380-420	408	84	9.00	9.07		Argon
	588-725	688	193	26.70	26.38		
				52.30	55.61	$\text{Cr}_2\text{O}_3\text{Cl}_2$	
	293-380	358	54	8.14	9.07		
	380-450	395	67	8.00	9.07		Air
	580-675	665	192	43.92	44.06		
	675-720	690	194	39.23	37.80	$\text{Cr}_2\text{O}_3$	
	303-368	343	57	9.45	8.76		
	438-525	478	83	9.84	8.76		Argon
2. $2 \text{CrIV} \text{O}_2 \text{Cl}_2 \cdot \text{Et}$ (Et = ethylbenzene)	588-720	668	157	29.70	28.86		
				51.00	53.64	$\text{Cr}_2\text{O}_3\text{Cl}_2$	
	298-365	335	44	9.41	8.76		
	370-440	393	59	8.16	8.76		Air
	570-680	663	191	42.47	45.94		
	680-725	698	192	39.11	36.56	$\text{Cr}_2\text{O}_3$	
	298-370	338	42	8.12	8.48		
	370-410	387	82	8.62	8.48		Argon
	575-728	698	158	30.09	31.18		
				51.53	51.87	$\text{Cr}_2\text{O}_3\text{Cl}_2$	
3. $2 \text{CrIV} \text{O}_2 \text{Cl}_2 \cdot n\text{P}$ (n-P = n-propylbenzene)	298-360	335	44	7.86	8.48		
	365-450	388	63	8.28	8.48		Air
	575-685	668	207	45.94	47.71		
	585-730	703	214	36.91	35.37	$\text{Cr}_2\text{O}_3$	

4. $2 \text{CrIV}_2\text{O}_2\text{Cl}_2 \cdot \text{iso-P}$ (iso-P = iso-propylbenzene)									
297-368	335	31	8.09	8.48					
368-415	393	69	9.32	8.48					Argon
588-725	688	143	32.83	31.18					
			49.18	51.89					$\text{Cr}_2\text{O}_3\text{Cl}_2$
300-350	328	39	8.72	8.48					
350-430	368	53	9.58	8.48					Air
565-670	658	169	45.72	47.71					
670-725	693	202	36.33	35.37					$\text{Cr}_2\text{O}_3$
5. $2 \text{CrIV}_2\text{O}_2\text{Cl}_2 \cdot \text{Ph}_2$ ( $\text{Ph}_2$ = diphenylmethane)									
298-375	328	53	6.87	7.60					
375-438	418	68	9.89	7.60					Argon
598-730	693	152	40.33	38.09					
			45.63	46.68					$\text{Cr}_2\text{O}_3\text{Cl}_2$
303-370	353	44	6.42	7.60					
370-450	393	58	8.50	7.60					Air
565-680	673	169	52.23	53.70					
680-730	698	171	32.84	31.82					$\text{Cr}_2\text{O}_3$

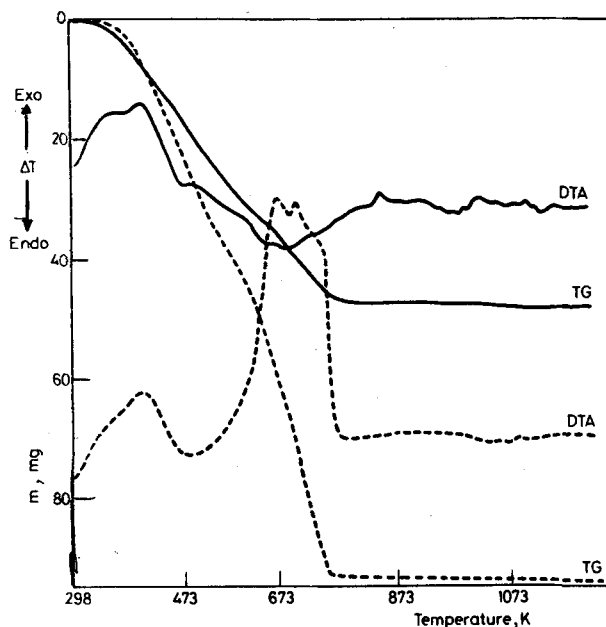
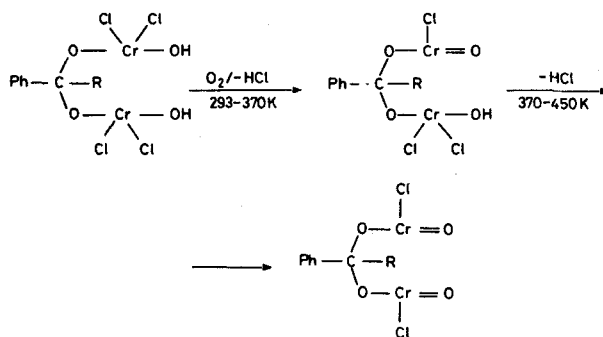
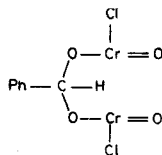


Fig. 1 Thermal curves for  $2\text{Cr}^{\text{IV}}\text{O}_2\text{Cl}_2 \cdot n\text{P}$ ; — argon atmosphere, - - - air atmosphere

thermic peaks in the DTA curves, also given in Table 1. The first decomposition stage occurs in the range 293–450 K and the DTA curve shows two overlapping peaks for the evolution of the two HCl molecules, as follows:



The sample weights in this mass loss step correspond almost exactly to the composition



in the case of the toluene product, but the content is a little smaller than the theoretical value. The intermediate is stable in the temperature range 450–580 K and decomposes abruptly at 665 K, with a weight loss of 43.92%. These exothermic processes are due to the oxidation reactions of the organic part of the molecules studied, leading to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{Cl}_2$  products. The final product of these reactions is  $\text{Cr}_2\text{O}_3$  and the mass of the samples attains the corresponding value at about 730 K.

### Chromium(IV) hydroxoacetates

The thermal curves of monochromium(IV) hydroxoacetate in argon and air atmospheres are shown in Fig. 2.

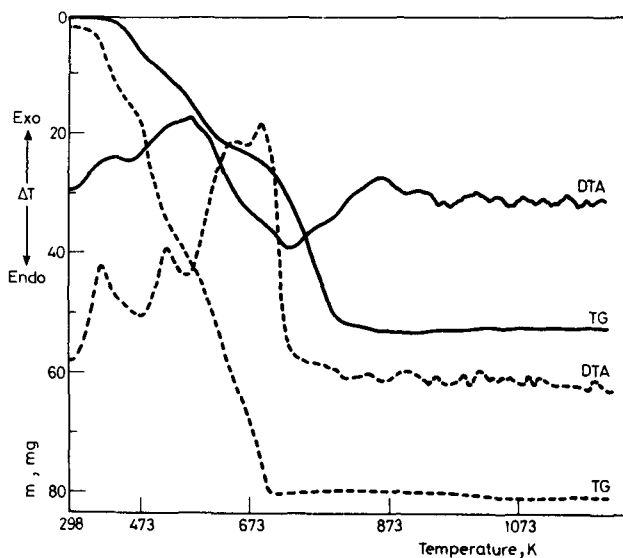
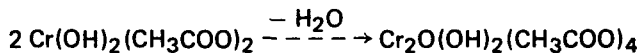


Fig. 2 Thermal curves for  $\text{Cr}(\text{OH})_2(\text{CH}_3\text{COO})_2$ ; — argon atmosphere, --- air atmosphere

The shape of the DTA in the inert atmosphere is very similar to those obtained for the chromyl chloride products. Chromium(IV) hydroxoacetate,  $\text{Cr}(\text{OH})_2(\text{CH}_3\text{COO})_2$ , loses half a water molecule at about 330 K, becoming dimeric in the reaction:



The intermediate,  $\text{Cr}_2\text{O}(\text{OH})_2(\text{CH}_3\text{COO})_4$ , decomposes rapidly in the second exotherm to give  $\text{Cr}_2\text{O}_3(\text{CH}_3\text{COO})_2$ . The weight loss of about 29% corresponds to two acetic acid molecules and the activation energy due to this process is about

Table 2 Results of thermal analysis of chromyl acetate products in argon and air atmospheres (monochromium(IV) hydroxoacetate)

Compound $\text{Cr}(\text{OH})_2(\text{CH}_3\text{COO})_2$	Range of temp., K	DTA peak temp., K	Activation energy, kJ/mol	Weight loss, %		Composition of residue	Atmosphere
				Observed	Theoretical		
1. From toluene reaction	303-373	333	47	7.83	8.82		
	373-583	498	102	28.69	29.41		Argon
	585-780	693	187	14.54	14.22		
				47.34	48.04	$\text{Cr}_2\text{O}_3(\text{CO}_3)$	
	303-473	340	48	8.25	8.82		
	473-575	538	130	15.99	-		Air
	575-670	648	191	9.55	-		
	670-755	698	196	25.74	-		
				40.44	37.24	$\text{Cr}_2\text{O}_3$	
2. From ethylbenzene reaction	300-370	330	48	8.92	8.82		
	370-585	497	103	28.18	29.41		Argon
	585-780	690	189	13.26	14.22		
				48.83	48.04	$\text{Cr}_2\text{O}_3(\text{CO}_3)$	
	300-475	338	46	6.99	8.82		
	475-573	535	127	17.62	-		Air
	573-670	645	189	10.12	-		
	670-750	698	194	23.34	-		
				36.82	37.24	$\text{Cr}_2\text{O}_3$	
3. From <i>n</i> -propylbenzene reaction	300-370	334	46	7.72	8.82		
	370-580	495	101	28.10	29.41		Argon
	580-780	690	185	13.08	14.22		
				50.57	48.04	$\text{Cr}_2\text{O}_3(\text{CO}_3)$	
	300-473	342	45	7.83	8.82		
	473-580	540	129	16.75	-		Air
	580-670	648	193	9.34	-		
	670-760	698	195	26.82	-		
				39.23	37.24	$\text{Cr}_2\text{O}_3$	



4. From iso-propylbenzene reaction	300-365	330	47	10.52	8.82	Argon
	370-585	495	100	30.52	29.41	
	585-780	692	189	13.08	14.22	
				48.15	48.04	Cr <sub>2</sub> O <sub>3</sub> (CO <sub>3</sub> )
	298-475	340	47	7.92	8.82	Cr <sub>2</sub> O <sub>3</sub>
	475-580	538	127	15.63	-	
	580-670	646	192	10.21	-	
	670-766	698	195	25.63	-	
				40.03	37.24	
	5. From diphenylmethane reaction	300-370	335	45	7.44	8.82
370-580		500	99	27.23	29.41	
580-775		696	185	15.84	14.22	
				50.00	48.04	Cr <sub>2</sub> O <sub>3</sub> (CO <sub>3</sub> )
298-470		338	44	9.15	8.82	Cr <sub>2</sub> O <sub>3</sub>
470-580		539	122	16.84	-	
580-668		648	190	8.53	-	
668-760		698	199	27.16	-	
				38.17	37.24	
6. From triphenylmethane reaction		300-375	335	45	8.52	8.82
	375-580	503	102	26.87	29.41	
	580-770	695	189	13.08	14.22	
				48.32	48.04	Cr <sub>2</sub> O <sub>3</sub> (CO <sub>3</sub> )
	295-470	340	49	10.32	8.82	Cr <sub>2</sub> O <sub>3</sub>
	470-575	540	119	14.73	-	
	575-675	648	184	10.13	-	
	675-758	698	192	26.16	-	
				39.14	37.24	

102 kJ/mol (see Table 2). The next DTA endotherm is connected with the further decomposition to acetone and  $\text{Cr}_2\text{O}_3(\text{CO}_3)$  molecules. The residue after pyrolysis contains chromium(III) oxide.

As can be observed from Table 2, all the solids obtained in the reactions of chromyl acetate and alkylaromatics studied in this paper seem to be the same. Some small differences in the mass loss percentages in the partial steps are very probably due to the not precisely executed measurements as well as to the precision of the method of calculations.

The DTA curve of monochromium(IV) hydroxoacetate in air atmosphere shows four steps of decomposition: a dehydration step at 340 K, with an activation energy of about 47 kJ/mole; the loss of the second water molecule; the last two steps being the gradual decomposition of the intermediate to  $\text{Cr}_2\text{O}_2(\text{CO}_3)_2$  with evolution of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  molecules. These two processes are to be seen as two overlapping exotherms with  $T_m = 648$  and 698 K, respectively. The final product,  $\text{Cr}_2\text{O}_3$ , becomes stable at about 900 K. Because of the overlapping of the decomposition processes, it was impossible to estimate the appropriate amounts of the individual decomposition products.

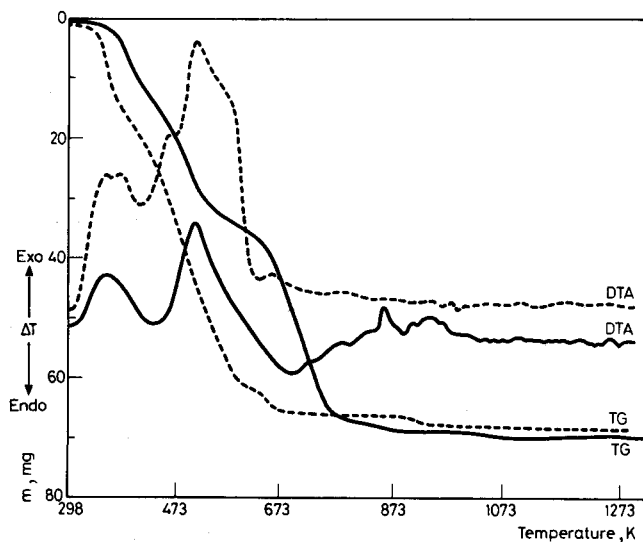


Fig. 3 Thermal curves for  $\text{Cr}_2\text{O}_2(\text{OH})_4(\text{CH}_3\text{COO})_2$ ; — argon atmosphere, - - - air atmosphere

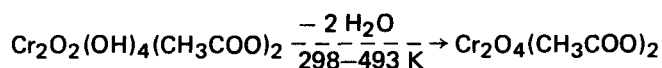
Table 3 and Fig. 3 show the thermal analysis results of dichromium(IV) hydroxoacetate in argon and air atmospheres. In the argon atmosphere the DTA curve exhibits two exothermic maxima, at 323 and 528 K, corresponding to dehydration and deacidification processes, respectively. The endothermic DTA peak at 688 K is due to

**Table 3** Results of thermal analysis of dichromium(IV) hydroxoacetate in argon and air atmospheres

Compound Cr <sub>2</sub> O <sub>2</sub> (OH) <sub>4</sub> (CH <sub>3</sub> COO) <sub>2</sub>	Range of temp., K	DTA peak temp., K	Activation energy, kJ/mol	Weight loss, %		Composition of residue	Atmosphere		
				Observed	Theoretical				
1. From toluene reaction	293–418	323	35	6.92	5.50	Cr <sub>2</sub> O <sub>3</sub>	Argon		
	418–648	528	125	19.14	—				
	648–853	688	193	19.28	18.01				
				50.28	47.20				
	2. From ethylbenzene reaction	298–373	353	47	7.25	5.50	Cr <sub>2</sub> O <sub>3</sub>	Air	
		373–493	410	72	9.13	5.50			
		493–555	530	131	24.75	41.60			
		555–703	578	125	14.65	—			
					50.54	47.20			
		3. From <i>n</i> -propylbenzene reaction	298–423	323	39	4.67	5.50	Cr <sub>2</sub> O <sub>3</sub>	Argon
			423–643	533	126	19.02	—		
			643–853	688	203	20.89	18.01		
					46.76	47.20			
4. From diphenylmethane reaction			298–370	353	47	7.53	5.50	Cr <sub>2</sub> O <sub>3</sub>	Air
			370–493	415	65	8.68	5.50		
			493–553	535	135	22.83	41.60		
	553–703		578	121	15.62	—			
					49.65	47.20			
	5. From <i>n</i> -propylbenzene reaction		295–420	323	37	5.70	5.50	Cr <sub>2</sub> O <sub>3</sub>	Argon
			420–640	530	124	19.92	—		
			640–850	690	200	20.67	18.01		
					48.69	47.20			
		6. From diphenylmethane reaction	298–373	353	49	6.63	5.50	Cr <sub>2</sub> O <sub>3</sub>	Air
			373–495	413	66	9.23	5.50		
			495–553	533	133	26.81	41.60		
553–698			578	124	13.17	—			
					49.63	47.20			
7. From diphenylmethane reaction			298–420	323	36	4.27	5.50	Cr <sub>2</sub> O <sub>3</sub>	Argon
			420–638	528	124	20.09	—		
			638–853	688	196	20.62	18.01		
					48.41	47.20			
	8. From diphenylmethane reaction		298–373	350	51	7.02	5.50	Cr <sub>2</sub> O <sub>3</sub>	Air
			373–488	410	64	8.75	5.50		
			488–550	530	134	23.72	41.60		
		550–703	575	122	14.13	—			
					48.75	47.20			

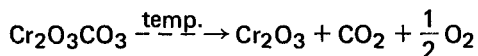
the separation of acetone produced in the decomposition of acetate anions. The final weight of about 47% corresponds to chromium(III) oxide. The activation energies for the decomposition processes seem to be the same in all presented cases (see Table 3).

The decomposition behaviour of dichromium(IV) hydroxoacetate in air atmosphere was found to be very similar to that of monochromium(IV) hydroxoacetate. The first two overlapping exotherms are the result of dehydration of the studied molecule:



The higher than theoretical weight loss percentage and the activation energy of about 65 kJ/mol instead of 37 kJ/mol are results of the further decomposition of the intermediate Cr<sub>2</sub>O<sub>4</sub>(CH<sub>3</sub>COO)<sub>2</sub> to Cr<sub>2</sub>O<sub>3</sub>(CO<sub>3</sub>) in the temperature range 493–703 K,

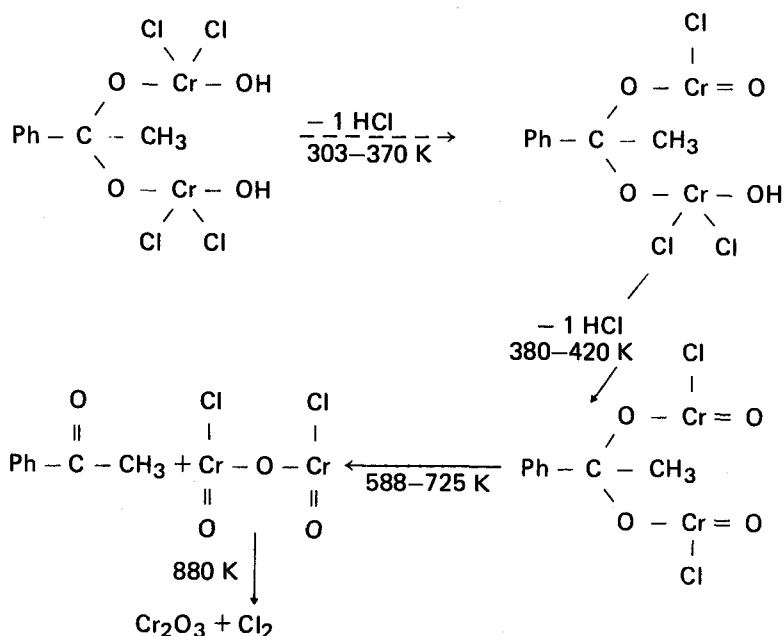
with two overlapping exothermic maxima at 530 and 578 K.  $\text{Cr}_2\text{O}_3$  arises in the decomposition process in the following reaction



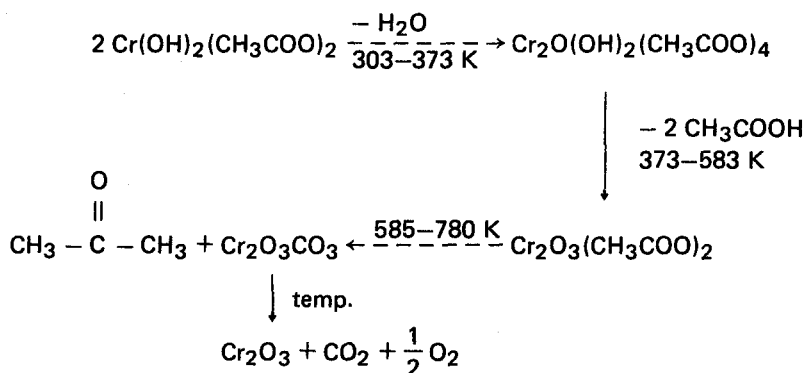
### Conclusions

The presented paper includes thermal analysis results on 15 solid products of the reactions of chromyl chloride and chromyl acetate with alkylaromatics. The measurements were performed in inert and air atmospheres.

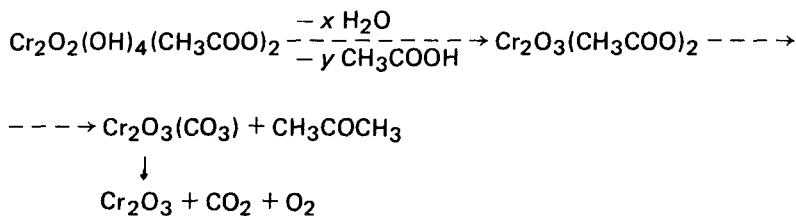
The results of the thermogravimetric investigations on the chromyl chloride products in argon atmosphere indicate that the thermal decomposition of these compounds involves two exotherms and one endotherm, corresponding to the evolution of two HCl molecules and then a ketone molecule, respectively. We propose the following decomposition steps for this type of complexes:



DTA curve analysis on  $\text{Cr}(\text{OH})_2(\text{CH}_3\text{COO})_2$  in an argon atmosphere indicates the existence of an intermediate with the formula  $\text{Cr}_2\text{O}(\text{OH})_2(\text{CH}_3\text{COO})_2$ , and the corresponding processes of decomposition can be described as follows:

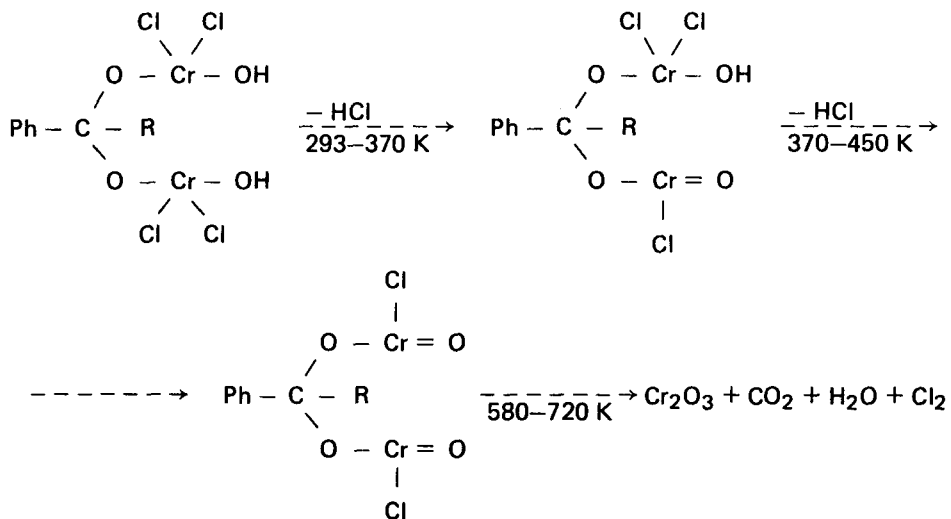


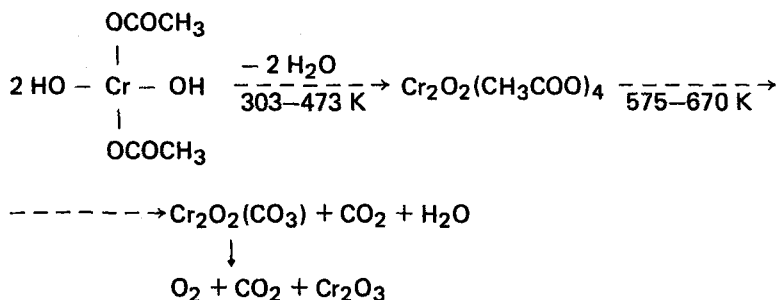
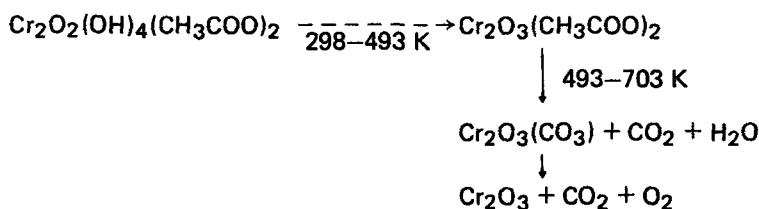
On the basis of thermogravimetric studies of dichromium(IV) hydroxoacetate, we propose the following decomposition process (in argon atmosphere):



For the thermal investigations of the compounds studied in air atmosphere we assumed the following decomposition paths:

#### Chloride compounds



*monochromium(IV) hydroxoacetate**and dichromium(IV) hydroxoacetate*

It should be noted that the DTA curves of all the compounds studied in air atmosphere show exothermic peaks which must be associated with oxidation processes of the starting materials.

The expected decompositions of the complexes in argon atmosphere are via the ketones. We obtained  $\text{Cr}_2\text{O}_3$  as final product even in air atmosphere. The  $\text{CrO}_3$  expected under oxidation conditions is stable only to 560 K, and it decomposes further to  $\text{Cr}_2\text{O}_3$  and  $\text{O}_2$ .

It appears from the presented Tables 1–3 that the activation energy values do not vary much with the change of the hydrocarbon and those of the acetates are nearly the same. It is interesting to note that the ratio of the  $E_a$  values calculated from the simplified Piloyan relation is very similar for all the acetates, while for the chloride complexes it decreases when the hydrocarbon is changed from toluene to diphenylmethane.

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**Zusammenfassung** — Die thermische Zersetzung von 15 festen Produkten der Reaktionen von Chromylchlorid und Chromylacetat mit Alkylaromaten wurde mittels eines Derivatographen in Argon- und Luftatmosphäre untersucht. Im Falle der Chromylchloridkomplexe  $2 \text{Cr}^{\text{IV}}\text{O}_2\text{Cl}_2 \cdot \text{HR}$  (HR = Kohlenwasserstoffmolekül) wurde in inerter Atmosphäre die Bildung von  $\text{Cr}_2\text{O}_3\text{Cl}_2$  als instabiles Zwischenprodukt beobachtet, während in Luft die abrupte Zersetzung der Komplexe zu  $\text{Cr}_2\text{O}_3$  als Rückstand führt. Die Zersetzung des Monochrom(IV)-hydroxyacetats und des Dichrom(IV)-hydroxyacetats verläuft sowohl in Argon- als auch in Luftatmosphäre über das Zwischenprodukt  $\text{Cr}_2\text{O}_3(\text{CO}_3)$ . Die charakteristischen Temperaturen werden diskutiert und in allen Fällen wurden die Aktivierungsenergien  $E_a$  der einzelnen Zersetzungsschritte berechnet.

**Резюме** — С помощью дериватографа изучено в атмосфере воздуха и аргона термическое разложение 15 твердых продуктов реакции хромил хлорида и хромил ацетата с алкилароматическими соединениями. При разложении комплексов с хромил хлоридом типа  $2 \text{Cr}^{\text{IV}}\text{O}_2\text{Cl}_2 \cdot \text{HR}$  где HR — молекула ароматического углеводорода, в инертной атмосфере наблюдалось образование неустойчивости промежуточного продукта  $\text{Cr}_2\text{O}_3\text{Cl}_2$ , тогда как в атмосфере воздуха — происходит резкое разложение комплексов с образованием  $\text{Cr}_2\text{O}_3$  в качестве конечного продукта реакции. Разложение моно- и дихром(IV) гидроксидоацетатов в атмосфере воздуха и аргона протекает через стадию образования промежуточного продукта  $\text{Cr}_2\text{O}_3(\text{CO}_3)$ . Обсуждены характерные температурные и вычислены энергии активации  $E_a$  отдельных стадий разложения.