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THERMAL DECOMPOSITION OF Cr(III) COMPLEXES WITH UREA AND THIOUREA

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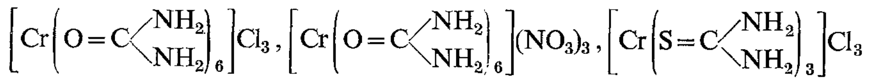
The thermal decompositions of Cr(III) complexes with urea and thiourea were investigated. The courses of the decompositions were found to be anion- and ligand-dependent. Suggestions for a mechanism of decomposition of these complexes are presented. The final product of decomposition of the complexes investigated was chromium(III) oxide (Cr_2O_3).

Cr(III) complexes with urea and thiourea have been known for a long time [1, 2]. Their structures have been studied by Penland and co-workers [3]. They have been obtained in low yields by the Pfeiffer [2] method. We have developed a simple and efficient method for obtaining these complexes, which was reported separately [4]. The present paper deals with the study of the thermal decompositions of the following complexes:



$$\left[\mathrm{Cr}\left(\mathrm{O}=\mathrm{C}\genfrac{}{}{0pt}{}{\diagup \mathrm{NH_2}}{\diagdown \mathrm{NH_2}}\right)_6\right]\mathrm{Cl_3},\ \left[\mathrm{Cr}\left(\mathrm{O}=\mathrm{C}\genfrac{}{}{0pt}{}{\diagup \mathrm{NH_2}}{\diagdown \mathrm{NH_2}}\right)_6\right](\mathrm{NO_3})_3,\ \left[\mathrm{Cr}\left(\mathrm{S}=\mathrm{C}\genfrac{}{}{0pt}{}{\diagup \mathrm{NH_2}}{\diagdown \mathrm{NH_2}}\right)_3\right]\mathrm{Cl_3}$$

Experimental

The complexes obtained by our method were dried at room temperature over P_2O_5 under reduced pressure, then analyzed. Table 1 shows the analyses of the complexes investigated.

The experiments were carried out with a Paulik—Paulik—Erdey Model Derivatograph (MOM, Budapest). The measuring conditions were the following: heating rate 10°/min, reference material: Al_2O_3, platinum crucibles, air atmosphere.

Results and discussion

Fig. 1 shows the thermal curves of the chromium nitrate complex with urea. The first mass loss began at about 170°; after melting (at about 200°) the sample underwent vigorous decomposition accompanied by a strong exothermic effect with a maximum at 235°. Above this temperature, and up to 500° at the end of the measurement, the mass loss progressed very slowly and reached about 4.5% of the initial sample mass, whereas during the main decomposition stage it had reached 80% of the sample mass.

This loss corresponds almost exactly to that of urea and nitrate anions, but not to that of the oxygen required for the formation of Cr_2O_3 which, as results from the mass of the residue after completion of the measurement (14%), is the final decomposition product (theoretical content of Cr_2O_3 = 12.8%). The exothermic effect at 445° can be ascribed to the formation of Cr_2O_3.

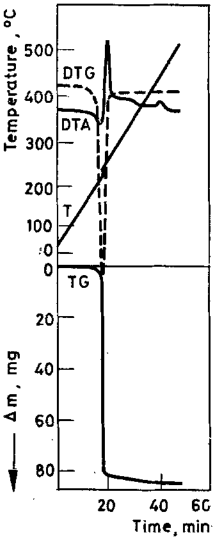


Fig. 1. TG, DTG and DTA curves of the chromium nitrate complex with urea

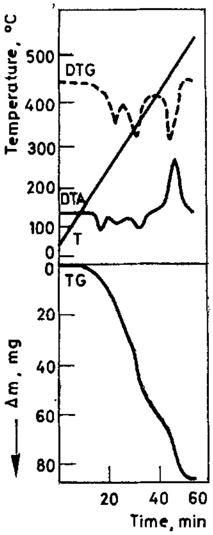


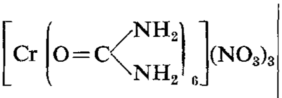
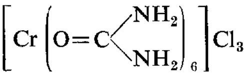
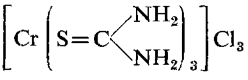
Fig. 2. TG, DTG and DTA curves of the chromium chloride complex with urea

Fig. 2 shows the thermal analysis of the chromium chloride complex with urea. Decomposition began at about 170° and went on at an increasing rate after melting of the sample at 195°. Analysis of the DTG and TG curves revealed splitting-off of two urea molecules in the range 170–280°. The corresponding endothermic effect occurred at 265°. The four remaining urea molecules split off in the range 280–450°, this finding reflection in the DTA endothermic effect at 332°.

The results obtained cannot serve as the basis for determining the exact initial temperature at which chloride is split off but, as can be seen from the differing TG fragment, the splitting-off of chloride begins below 450° and occurs up to 480°. This was corroborated by additional analyses of samples in which the chloride content had been determined, and which were heated in the range 230–330°. At temperatures above 480° and up to 525° at the end of the measurement, the sample mass remained almost unchanged.

Table 1

Analytical data of Cr(III) complexes with urea and thiourea

Complex	Chromium, %		Carbon, %		Hydrogen, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
 $[Cr(O{=}C(NH_2)_2)_6](NO_3)_3$	8.66	8.63	12.01	12.30	4.01	4.12
 $[Cr(O{=}C(NH_2)_2)_6]Cl_3$	10.03	9.98	13.90	13.60	4.62	4.63
 $[Cr(S{=}C(NH_2)_2)_3]Cl_3$	13.46	13.24	9.36	9.16	3.12	3.23

The mass of the residue (14.5%) corresponds exactly to the mass of Cr_2O_3 which can be obtained on decomposition of the compound investigated (14.7%). The pronounced exothermic effect with a maximum at 460° can be ascribed to the formation of Cr_2O_3.

Analyses of the chromium chloride complex with thiourea are shown in Fig. 3. As can be seen from these curves, decomposition starts at 220°, and melting at 245°. TG and DTG analyses indicated that the first thiourea molecule split off in the range of 222 to about 275°. This was associated with a strong exothermic effect

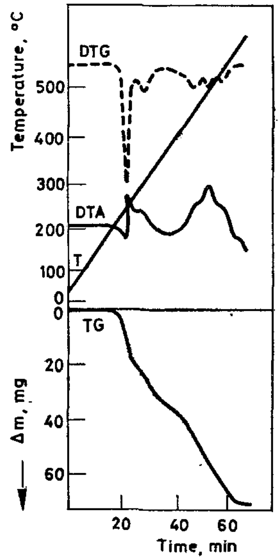


Fig. 3. TG, DTG and DTA curves of the chromium chloride with thiourea

at 260°. The splitting off of the second thiourea molecule at about 380° was also associated with an exothermic effect at 300°. The last thiourea molecule split off at temperatures up to 480°; an exothermic effect was observed at 460°.

Determination of chlorine in a sample subjected to roasting at 330° showed that chlorine splits off above that temperature. This established that the last TG section (up to about 540°) corresponds to chlorine evolution. The pronounced exothermic effect with a maximum at 495° can be ascribed to the formation of Cr_2O_3. The mass of the residue (22.5%) after completion of the measurement at 580° corresponds approximately to the theoretical Cr_2O_3 content of the sample (19.7%).

Conclusions

The above investigations allowed determination of the stages and the mechanism of the decomposition of the compounds studied.

The course of the decomposition of Cr(III) complexes with urea was found to be dependent on the anion bound to the complex. In the case of the nitrate anion, decomposition occurred very violently in one single stage, whereas in the case of the chloride anion, decomposition occurred in a multistage process.

Thermal analysis of chloride complexes with urea and thiourea has shown that organic ligands split off in the first decomposition stage, and chlorine in the last.

The final decomposition product of all three complexes investigated was chromium(III) oxide, Cr_2O_3.

References

1. A. Werner and D. Kalkmann, Ann., 322 (1902) 313.
2. P. Pfeiffer, Ber., 36 (1903) 1926.
3. R. B. Penland, S. Mizushima and J. V. Quagliano, J. Am. Chem. Soc., 79 (1957) 1575.
4. B. Bator-Sawicka, G. Błotny and J. Dobrowolski, Roczniki Chem., 49 (1975) 829.

Résumé — On a étudié la décomposition thermique des complexes du chrome(III) avec l'urée et la thiourée. On a trouvé que le processus de la décomposition dépend de l'anion et du ligand. On propose un mode de décomposition mécanique pour ces complexes. Le produit final de la décomposition des complexes étudiés est l'oxyde de chrome(III), Cr_2O_3.

Zusammenfassung — Die thermische Zersetzung der Komplexe von Cr(III) mit Karbamid und Thiokarbamid wurde untersucht. Der Verlauf der Zersetzung wurde für Anionen- und Liganden-abhängig gefunden. Vorstellungen über eine mechanische Zersetzung dieser Komplexe werden gegeben. Das Endprodukt der Zersetzung der untersuchten Komplexe war jeweils Chrom(III)oxid (Cr_2O_3).

Резюме — Исследовано термическое разложение комплексов Cr (111) с мочевиной и тиомочевиной. Было найдено, что ход разложения комплексов зависит от природы аниона и лиганда. Представлены предположения о механизме разложения этих комплексов. Конечным продуктом разложения исследованных комплексов является окись хрома (111) (Cr_2O_3).