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STUDIES ON THE THERMAL DECOMPOSITIONS OF AS-TRIAZINE DERIVATIVES AND THEIR COMPOUNDS WITH METAL IONS

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The thermal decompositions of the new complex salts of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 5,6-diethoxycarbonylmethyl-3-seleno-1,2,4-triazine (HSeTEK) and 5,6-diethoxycarbonylmethyl-3-thio-1,2,4-triazine (HTTEK) were investigated on the basis of the respective thermal curves. The thermoanalytical investigations indicate that HSeTEK, HTTEK, and their complexes with metal ions all undergo three-stage changes as the temperature is raised. The stages of pyrolysis established from the thermal data were compared, and the rates and stages of pyrolysis were related to the structures of the compounds.

Our earlier investigations [1–4] have shown that two new biologically active derivatives of as-triazine (Fig. 1) readily form crystalline precipitates with some metal ions. We have obtained Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of HSeTEK and HTTEK, i.e. the compounds presented in Fig. 1. The chemical compositions of these complexes were established by elementary analysis methods [4]. This paper presents the results of the thermal analysis of the complexes.

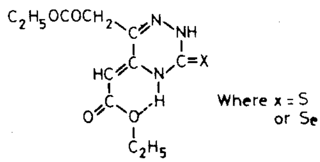

Fig. 1 as-Triazine derivatives, i.e.: 5,6-diethoxycarbonylmethyl-3-seleno-1,2,4-triazine (HSeTEK) or 5,6-diethoxycarbonylmethyl-3-thio-1,2,4-triazine (HTTEK), where X = Se or S

Experimental

The complexes were purified by boiling in a water-methanol solution, and they were subsequently air-dried. The thermoanalytical curves were obtained with a

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Q1500 D derivatograph. The thermal decompositions of the samples were carried out in their own atmospheres. Samples were heated from 20° up to 1000° at a heating rate of 5 deg/min. α-Al_2O_3 was the reference material.

Results, discussion and conclusions

Our thermoanalytical investigations (Figs 2–4 and Tables 1–4) indicate that HSeTEK, HTTEK and their complexes with metal ions all undergo three-stage changes as the temperature is raised. The first stage is connected with physicochemical changes and with the liberation of the weakly bound water molecules. The TG curves indicate rather small mass decrements, which are accompanied by endothermic changes. We have ascribed these mass losses to the liberation of one molecule of water from the complex compound molecule. This is illustrated by the data in Table 1; on the basis of these data, it was assumed that the Mn(II), Co(II), Cu(II) and Zn(II) complexes contain two water molecules each. The second stage of decomposition occurs within the range 200–370°. Large mass losses and weak exothermic changes are observed here. The third stage is characterized by strong exothermic changes and large mass losses. In the final phase of this stage, the TG curves of the complexes reveal characteristic decreases of mass, which can be taken to mean that the oxidation of the sulphide or selenide of the metal to a

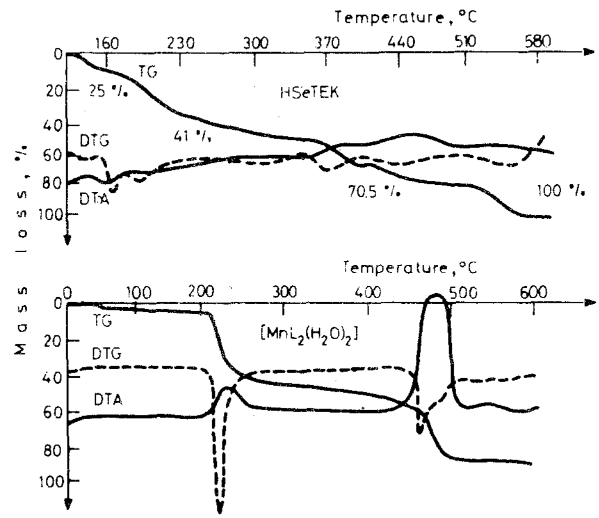

Fig. 2 Thermal decomposition curves of HSeTEK and of its complexes with Mn(II), L = indicates the $SeTEK^-$ anion

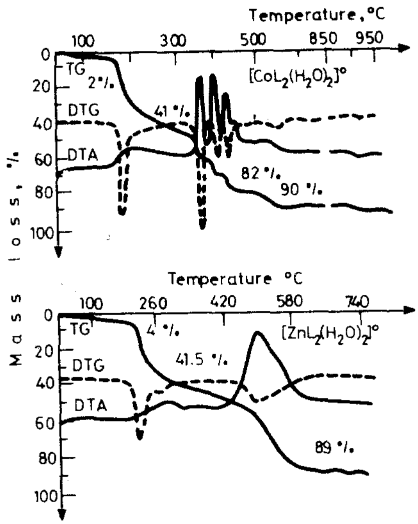

Fig. 3 Thermal decomposition curves of Co(II) and Zn(II) complexes with HSeTEK, L = indicates the $SeTEK^-$ anion

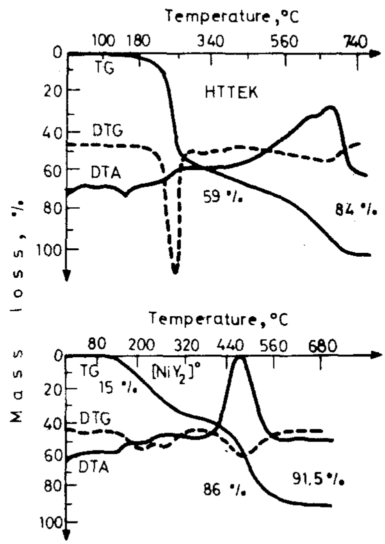

Fig. 4 Thermal decomposition curves of HTTEK and its Ni(II) complex. L = indicates the $TTEK^-$ anion

Table 1 Observed and calculated mass loss of samples of complex compounds caused by liberation of one H_2O molecule* at heating within the 20–205° range

Molecular formula	Molecular mass	Mass loss, %		DTG peak temperature, °C
		observed	calculated	
$[MnL_2(H_2O)_2]$	(753)	2.5	2.4	55
$CoL_2(H_2O)_2$	(757)	2.0	2.4	70
NiL_2	(723)	0.3	—	—
$CuL(H_2O)_2CH_3COO$	(489)	4.0	3.7	55
$ZnL_2(H_2O)_2$	(763)	4.0	4.7	205
$CoY_2(H_2O)_2$	(663)	3.0	2.7	78
NiY_2	(627)	—	—	—
$CuY(H_2O)_2CH_3COO$	(442)	3.0	4.0	50
$ZnY_2(H_2O)_2$	(669)	4.0	4.7	180

* in this temperature range Zn(II) complexes liberate two H_2O molecules at a time; L – SeTEK, Y – TTEK.

corresponding oxide occurs. Table 2 presents the thermal decomposition process proposed on the basis of the TG and DTA curves. Since the area of a DTA peak is proportional to the thermal effect of a process, the areas of corresponding DTA peaks were measured in order to examine the influence of the metal ion in the complex. The effects of the metal ions on the relative amount of heat in stage III and on the total amount of heat emitted in stages II and III are illustrated in Fig. 5. The

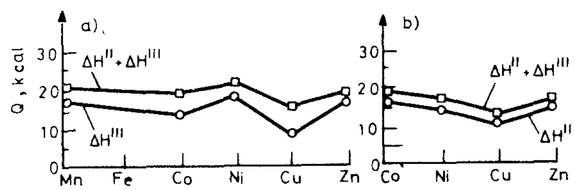

Fig. 5 The effect of metal ion atom number Z on the relative amount of heat emitted (Q) in the III. and in the II. and III. stages of the thermal decomposition of the a) HSeTEK complexes and b) HTTEK complexes

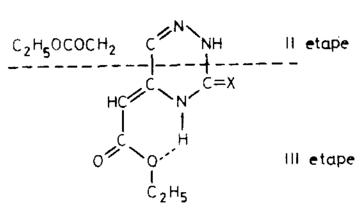

Fig. 6 The scheme of thermal decomposition of the ligand molecules

Table 2 Observed and calculated mass loss (%) during the second and the third stage of decomposition of HSeTEK, HTTEK and their complexes with metal ions

Compound	II. stage of decomposition			III. stage of decomposition		
	Temperature range, °C	Mass loss, % observed	Mass loss, % calculated	Temperature range, °C	Mass loss, % observed	Mass loss, % calculated
HSeTEK	160–235	41.0	38.5	235–650	100.0	100.0
$MnL_2(H_2O)_2$	210–250	40.0	38.6	250–580 MnO remains	90.5	90.6
$CoL_2(H_2O)_2$	180–265	41.0	38.5	265–1000 CaO remains, i.e. 9.8%	91.0	90.3
NiL_2	170–325	33.5	35.5	325–610 NiO remains, i.e. 12.5%	87.5	87.6
$CuL(H_2O)_2CH_3COO$	20–260 the first and the second stage of decomposition	44.0	45.6	260–610 CuO remains, i.e. 16.2%	81.5	83.8
$ZnL_2(H_2O)_2$	205–320	41.5	38.2	320–610 ZnO remains, i.e. 10.6%	89.0	89.5
HTTEK	185–285	55	44.9	285–640	100.0	100.0
$CoY_2(H_2O)_2$	200–290	43.0	44.0	290–940 CaO remains, i.e. 11.3%	90.0	88.7
NiY_2	165–410	41.0	40.8	410–600 NiO remains, i.e. 11.9%	91.5	88.1
$CuY_2(H_2O)_2CH_3COO$	140–275	37.0	37.0	275–770 CuO remains, i.e. 16.2%	81.5	83.8
$ZnY_2(H_2O)_2$	205–320	41.5	38.2	320–910 ZnO remains, i.e. 10.6%	89.0	89.5

Table 3 Characterization of the II. stage of thermal decomposition of HSeTEK and its complexes with metal ions

Compound	Tempera-ture range, °C	The observed process and temperature for DTA peak, °C	Mass loss, %	
			observed	calcu-lated
HSeTEK (SeTEK = L)	160–235	80°-liberation of N_2 from the heterocyclic ring 210°-oxidation of the first part	9.5	8.4
$MnL_2(H_2O)_2$	210–250	235°-liberation of the second H_2O molecule and oxidation of the first part of ligand groups	40.0	28.6
$CoL_2(H_2O)_2$	180–265	205°-liberation of the second H_2O molecule and oxidation of the first part	41.0	38.5
NiL_2	170–325	285°-multi-staged decomposition of the first part of both ligand groups	33.5	35.5
$ZnL_2(H_2O)_2$	205–320	220–285°-oxidation of the first part of both ligand groups	41.5	38.2
$CuL(H_2O)_2CH_3COO$	20–260	55°-liberation of one H_2O molecule	4.0	3.7
		170°-liberation of the second H_2O molecule	9.0	7.3
		230°-decomposition of the acetate ion and of the first part of the ligand		

curves presented in this Figure indicate that the metal ion exerts a slight effect on the amount of heat Q emitted in stage II or III of the thermal decomposition. This is justifiable if it is assumed that decomposition of the same fragment of ligands occurs in both stages. Complexes with two $SeTEK^-$ or $TTEK^-$ ions should have roughly twice as large heats of decomposition (ΔH) as the 1 : 1 complexes, but since the latter complexes contain acetate ion (see Table 1), this does not hold rigorously; this is illustrated by the $\Delta H^{II} + \Delta H^{III}$ curves in Fig. 5. The data obtained reveal that the thermal decompositions of the ligand molecules and of the complex molecules always cause oxidation of the same fragments of the ligand molecule in the second and third stages of the oxidation, which can be illustrated by the scheme shown in Fig. 6. In the final products of decomposition of the complexes, oxides of the relevant metals were identified.

Table 4 Characterization of the III. stage of thermal decomposition of HSeTEK and its complexes with metal ions

Compound	Temperature range, °C	The observed process and temperature for DTA peak, °C	Mass loss, %	
			observed	calculated
HSeTEK	235–650	370°-oxidation of the CNSe	70.5	70.0
		440°-liberation of CO_2	82.5	83.2
		560°-oxidation of remainders	100.0	100.0
$MnL_2(H_2O)_2$	250–580	550°-oxidation of the second part ligands, MnO remains 9.4% compound	90.5	90.6
$CoL_2(H_2O)_2$	265–1000	some peaks decomposition of the second of ligands with formation CoSe	82.0	81.8
		517°—CoSe → Co_2O_3	90.0	89.3
		910°—Co_2O_3 → CoO remains CoO i.e. 9.8% compound	91.0	90.3
NiL_2	325–610	497°-decompósition of the remained ligands with formation NiSe	79.5	81.1
		570°—NiSe → NiO remains NiO i.e. 12.5% compound	87.5	87.6
$ZnL_2(H_2O)_2$	320–610	510°-oxidation of the seond part ligands, ZnO remains, i.e. 10.6% związku	89.0	89.5
$CuL(H_2O)_2CH_3COO$	260–610	440°-oxidation of the second part ligand with formation CuSe	71.0	71.1
		595° CuSe → CuO remains CuO, i.e. 16.2% compound	81.5	83.8

References

1 J. Masłowska and J. Jaroszyńska, 7th International Symposium on Solute-Solute-Solvent Internations, 15–19th July 1985 University of Reading, Great Britain,. Proceedings of the Symposium, Section 2, p. 13.

2 J. Jaroszyńska, Zeszyty Naukowe PŁ, Technologia i Chemia Spożywcza (Sci Bull of Łódź Techn. Univ., Production Technology and Food Chemistry), 39 (1985) 55.

3 J. Masłowska and J. Jaroszyńska, Polish J. Chem. (In press).

4 J. Masłowska and J. Jaroszyńska, Proceedings of the Scientific Session on the Occasion of the 35th Anniversary of the Faculty of Food Chemistry of the Technical University of Łódź, entitled: "Biotechnology and Food Chemistry" 1985, Łódź, Poland, pp. 96–101. (In Polish)

5 S. Nishigaki, M. Ichiba and K. Senga, J. Org. Chem., 48 (1983).
6 Ch. Tzeng, N. C. Motola and R. P. Panzica, J. Org. Chem., 48 (1983) 1271.
7 M. Negwer, Organisch Chemisch Arzneimittel und ihre Synonyma, Berlin 1971, Vol. 2, p. 12, 124, 350.
8 J. Masłowska and J. Jaroszyńska, J. Mol. Struct., (under publication).

Zusammenfassung — Die thermische Zersetzung der neuen Komplexsalze von Mn(II), Co(II), Ni(II) und Cu(II) mit 5,6-Diäthoxycarbonylmethyl-3-seleno-1,2,4-triazin (HSeTEK) und 5,6-Diäthoxycarbonylmethyl-3-thio-1,2,4-triazin (HTTEK) wurden auf der Grundlage der entsprechenden thermischen Kurven untersucht. Die thermoanalytischen Untersuchungen zeigen, daß HSeTEK, HTTEK und deren mit Metallionen gebildeten Komplexe bei Temperaturerhöhung einer jeweils dreistufigen Umwandlung unterliegen. Die auf der Basis der thermischen Daten festgestellten Pyrolysestufen wurden verglichen und Geschwindigkeit und Abschnitte der Pyrolyse mittels der Struktur der Verbindungen erläutert.

Резюме — Изучено термическое разложение новых комплексных солей марганца, кобальта, никеля и меди с 5,6-диэтоксикарбонилметил-3-селено-1,2,4-триазином и с 5,6-диэтоксикарбонилметил-3-тио-1,2,4-триазином. Термоаналитические исследования показали, что как свободные лиганды, так и их комплексы подвергаются трехступенчатому разложению. Отдельные стадии пиролиза и их скорости сопоставлены и связаны со структурой исследованных соединений.